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CHEMICAL ANALYSIS.

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LESSONS
IN
QUALITATIVE
CHEMICAL ANALYSIS

BY

Dr. F. BEILSTEIN,

PROFESSOR AT THE IMPERIAL INSTITUTE OF TECHNOLOGY
OF ST. PETERSBURG.

TRANSLATED FROM THE FIFTH EDITION, WITH COPIOUS ADDITIONS,
INCLUDING LESSONS IN ORGANIC AND IN
VOLUMETRIC ANALYSIS.

BY

CHARLES O. CURTMAN, M. D.,

PROFESSOR OF CHEMISTRY IN THE MISSOURI MEDICAL COLLEGE,
AND IN THE ST. LOUIS COLLEGE OF PHARMACY.

ILLUSTRATED.

SAINT LOUIS, MO.
ST. LOUIS STATIONERY & BOOK CO., PUBLISHERS,
405 & 407 N. FOURTH STREET.
1883.

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PREFACE.

The attractive manner of teaching chemical operations by examples, each one of which gives to the student the satisfaction of having made a complete analysis, has rendered Beilstein's "Anleitung" deservedly popular as a text-book in many institutions. It is intended to be an easy introduction to more elaborate work, and to be followed by the use of some of the larger manuals. Many of our medical and pharmaceutical colleges require a more extended laboratory course than the one given by Beilstein, yet do not go sufficiently far, to need the training necessary for professional chemists. Such is the case in my own classes, where Beilstein has been used as a text-book, and the supplementary work has been taught by oral instructions, accompanied by practical demonstrations, the students taking notes and using them as a guide to their work. This will answer where the instructor is well supplied with skilled assistants, otherwise it will limit the time that should be given to the close personal superintendence of each student's work. Misunderstandings and erroneous notes are now and then occurring and in case of unavoidable absence, the oral instruction cannot easily be supplied. I have therefore attempted in this little volume to join to a translation of Beilstein's latest edition an outline of such instructions, sufficiently extended and explicit to furnish the student with notes, which will obviate the necessity of continual applications to the teacher, yet leaving enough to his judgment, to stimulate him to independent effort.

It begins with instructions in the common manipulations of the laboratory. Then follow the "examples," which are increased in number, and so arranged as to place the reactions for bases and acids under separate headings, thereby making them more impressive. After the examples a short chapter is added giving instructions for systematic examination of substances containing a single base. This is intended to be used together with the examples in the following manner. As soon as the student has gone through the first fifteen examples, comprising the bases of the first and second groups, there are given to him specimens from among the substances studied and he is instructed to analyze them as directed on page 57, IV to VI. Again when example XXIII has been reached, other specimens (unknown to the student) are given him, containing one of the bases of groups III and IV, and he examines them according to page 56, III. This is again repeated after he has finished example XXXIII, when he has to examine specimens of the copper and arsenic groups according to page 54, I. After completing the examples, another examination takes place, in which specimens are furnished containing a single base of any of the six groups.

Next follows the systematic course, somewhat enlarged by a chapter on the use of the spectroscope, Marsh's arsenic test and other additions. This concludes the course given in the original. A few examples of qualitative analysis of organic substances are then added and lastly some practical instructions in volumetric analysis. Directions for making and using the standard solutions, and explanations of the chemical processes involved, are followed by examples for practice. Altogether the amount of material added has more than doubled the size of the original.

In selecting material from a field as well and thoroughly cultivated as chemical analysis, so much must be compiled from various sources, that it would be impossible to acknowledge in detail how much is due to each. The works of Rose, Fresenius, Will, Sonnenschein, Classen, Moore and Post, are among the many from which I have drawn. New reactions from the periodical literature have been verified by practical experiments, before finding a place in these pages. In the chapters on volumetric analysis especial reference is made to the standards of the new U. S. Pharmacopoeia.

CHAS. O. CURTMAN, M. D.

Saint Louis, Mo.
August 1, 1883.

CONTENTS.

PAGE.
Table of atomic weights..1
Relations of metric to U. S. measures and weights.............2

Chemical Manipulations.

1. Management of heat..3
2. Use of blow-pipe..6
3. Manipulation of glass tubing..............................8
4. Working with corks..10
5. Filtration..10
6. Miscellaneous notes.......................................13

Examples for practice in qualitative analysis.

I. Sodium chloride...15
II. Sodium carbonate...16
III. Sodium sulphate...17
IV. Potassium nitrate..17
V. Ammonium chloride...19
VI. Potassium and sodium tartrate............................20
VII. Sodium phosphate..20
VIII. Sodium diborate..21
IX. Magnesium sulphate.......................................22
X. Calcium carbonate...23
XI. Barium chloride..24
XII. Strontium chloride......................................24
XIII. Calcium sulphate.......................................25
XIV. Calcium phosphate.......................................26
XV. Calcium fluoride...26
XVI. Aluminium ammonium sulphate.............................27
XVII. Potassium dichromate...................................27
XVIII. Iron..29
XIX. Manganous sulphate......................................31
XX. Potassium permanganate...................................31
XXI. Zinc..32
XXII. Nickelous sulphate.....................................33
XXIII. Cobaltous nitrate.....................................33
XXIV. Lead...34
XXV. Lead acetate..35
XXVI. Bismuth..36

XXVII. Copper sulphate..36
XXVIII. Cadmium sulphate..37
XXIX. Mercury..38
XXX. Silver nitrate..39
XXXI. Tin..40
XXXII. Antimony..41
XXXIII. Arsenic and arsenic trioxide..42
XXXIV. Potassium chlorate..44
XXXV. Sodium silicate..45
XXXVI. Potassium acid oxalate..46
XXXVII. Sodium hyposulphite..47
XXXVIII. Potassium iodide..47
XXXIX. Potassium bromide..49
XL. Strontium sulphate..49
XLI. Barium sulphate..50
XLII. Potassium cyanide..51
XLIII. Lithium carbonate..51
XLIV. Commercial sulphuric acid..52
XLV. Gold chloride..52
Systematic examination of substances with a single base..54

Systematic course of qualitative analysis.

A PRELIMINARY EXAMINATION..59
I. Heating in glass-tube..59
II. Blowpipe tests on charcoal..60
III. Blowpipe tests on charcoal with Sodium carbonate...61
IV. Color of beads of microcosmic salt or borax..........61
V. Coloration of flame..63
VI. Use of the spectroscope..63
VII. Solution of the substance..65

B. DETECTION OF BASES.

General behaviour of the metals with the group reagents....67
First group, alkalies..68
Second group, alkaline earths..69
Third and fourth groups..70
    A. Chromium is absent..72
    B. Chromium is present..73
    C. Phosphates and oxalates of alkaline earths are present. 75
Fifth and sixth groups..77
  Fifth group..79

Sixth group.......81
  Second method for separating **As, Sn** and **Sb**.......83
  Third method for separating **As, Sn** and **Sb**.......84
  Detection of small quantities of arsenic by means of AsH_3..84
ANALYSIS OF COMPOUNDS INSOLUBLE IN WATER AND ACIDS..86
C. DETECTION OF ACIDS.......88
Classification of acids.......89
General properties of acids.......89
Examination for H_2SO_4, HCl, HNO_3, and H_3PO_4.......90
Examination for other acids.......91
ORGANIC ACIDS.......96
a. Preliminary tests.......96
b. Special reactions.......97
ANALYSIS OF SILICATES.......99
ANALYSIS OF CYANIDES.......102
Examples for practice in analysis of organic substances. 105
1. *Alcohol*.......105
2. *Chloroform*.......107
3. *Chloral hydrate*.......108
4. *Glucose*.......119
5. *Cane sugar*.......110
6. *Phenol*.......111
7. *Alkaloids*.......112
8. *Morphine*.......113
9. *Quinine*.......114
10. *Cinchonine*.......115
11. *Strychnine*.......115
12. *Atropine*.......116

Volumetric Analysis.

Introduction.......117
System of standard solutions.......118
Various methods of determination.......121
Indicators.......122
VOLUMETRIC INSTRUMENTS.......122
  A. Burettes.......122
  B. Pipettes.......125
  C. Measuring flasks.......126
CLASSIFICATION OF VOLUMETRIC PROCESSES.......127

ACIDIMETRY AND ALKALIMETRY.

Oxalic acid.......128

Sulphuric acid..129
Hydrochloric acid..129
Potassium hydrate..129
Sodium hydrate..131
Sodium carbonate..131
Ammonium hydrate..131
Barium hydrate..131
Saturation equivalents..132
Choice of indicator..133
Example 1. *Aqua ammoniae*..133
Example 2. *Sodium carbonate*..135
Example 3. *Acetic acid*..136
Example 4. *White wine*..137
Example 5. *Chloral hydrate*..137
OXIDIMETRY.
Potassium permanganate..138
Example 6. *Oxalic acid*..140
Example 7. *Ferric chloride*..141
Potassium dichromate..141
Example 8. *Ferrous sulphate*..142
IODIMETRY..143
Iodine..143
Sodium hyposulphite..144
Example 9. *Tinctura Iodi : U. S. P*..145
Example 10. *Liquor Potassii Arsenitis. U. S. P*..145
Example 11. *Liquor Sodae Chloratae. U. S. P*..145
PRECIPITATION ANALYSES.
Silver nitrate..146
Sodium chloride..147
Mercuric chloride..147
Example 12. *Potassium Cyanide*..147
Example 13. *Potassium Iodide*..148
Example 14. *Potassium Bromide*..148
Example 15. *Silver Nitrate*..159
SPECIAL VOLUMETRIC PROCESSES
Fehling's solution..150
Example 16. *Glucose*..151
Mercuric nitrate..153
Example 17. *Urea*..153
Example 18. *Phosphoric Acid*..154

Table of Atomic Weights. H = 1.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Li=7,01	Be=9,09	B=10,94	C=11,97	N=14,02	O=15,96	F=18,98	
Na=23	Mg=23,96	Al=27,01	Si=28,2	P=30,96	S=31,98	Cl=35,37	
K=39,02	Ca=39,99	Sc=43,98	Ti=49,85	Vd=51,26	Cr=52,01	Mn=53,91	Fe=55,91 Ni=57,93 Co=58,88
Cu=63,17	Zn=64,91	Ga=68,85	—	As=74,92	Se=78,8	Br=79,77	
Rb=85,25	Sr=87,37	Yt=89,82	Zr=89,37	Nb=94	Mo=95,53	—	Rh=104,06 Ru=104,22 Pd=105,74
Ag=107.68	Cd=111,77	In=113,4	Sn=117,7	Sb=119,96	Te=127,96	I=126,56	
Cs=132,6	Ba=136,76	La=138.53	Ce=140,42	Di=146,18	Tb=148,8	—	
—	—	—	—	Er=165,89	—	—	Ir=192,65 Pt=194,42 Os=198,49
—	—	Yb=172,76	—	Ta=182,14	W=183,61	—	
Au=196,16	Hg=199.71	Tl=203,72	Pb=206,47	Bi=207,52	Ng=214	—	
—	—	—	Th=233,41		Ur=238,48	—	

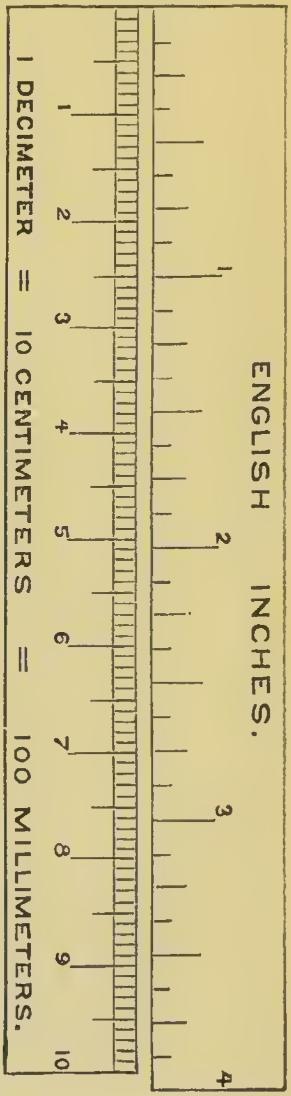
Relations of Metric to U. S. measures and weights.

The distance from the equator to the pole is divided into 10,000,000 meters. The divisions of the unit of measure or weight are indicated by the Latin numerals, the multiples by the Greek.

The unit of measure of length is 1 meter = 10 decimeters = 100 centimeters = 1000 millimeters. 10 meters = 1 decameter; 100 meters = 1 hectometer; 1000 meters = 1 kilometer.

1 meter = 39,37079 inches.
1 decimeter = 3,93708 inches.
1 centimeter = 0,39370 inches.
1 millimeter = 0,03937 inches.

1 inch = 25,3995 millimeters.



1 cubic centimeter of water at its point of greatest density weighs 1 gramme. 1 cubic decimeter = 1000 cubic centimeters = 1 litre. 1 litre water weighs 1 kilogramme = 2,6803 pounds troy = 2,20462 pounds avoirdupois.

The gramme is subdivided by the prefix of Latin, multiplied by that of the Greek numerals.

1 grain Troy weighs 64,799 milligrammes. 1 gramme = 15,43235 grains Troy. 1 gramme = 10 decigrammes = 100 centigrammes = 1000 milligrammes. 10 grammes = 1 decagramme; 100 grammes = 1 hectogramme; 1000 grammes = 1 kilogramme.

1 litre = 1000 cubic centimeters = 33,81 fluid ounces = 1,76 pints = 61,027 cubic inches. 1 cubic centimeter = 16,23 minims.

CHEMICAL MANIPULATIONS.

1. MANAGEMENT OF HEAT.

FOR the purposes of qualitative analysis heat is usually produced by gas lamps. Where coal gas is not obtainable, alcohol lamps may be used.

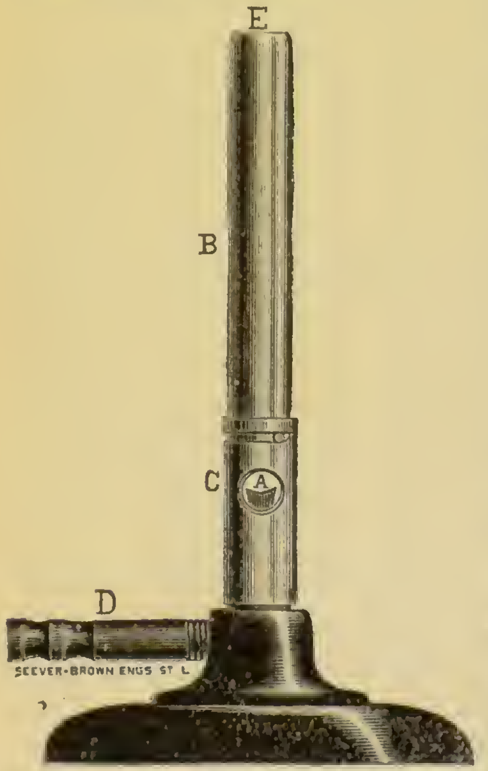


FIG. I.

The Bunsen Burner (fig. 1.) consists of a small burner (A) enclosed in a tube (B), open on top (E), to which air is admitted by round openings near the bottom of the tube. By turning a perforated collar (C), whose holes correspond with those in the tube, which it surrounds, the admission of air may be regulated and shut off entirely.

The supply of coal gas is admitted by the lateral tube (D), which is connected with the gas fittings of the laboratory by a rubber tube, and is regulated by an ordinary stopcock.

Exercises. Turn on the gas and light it at the top (E). Now turn the collar (C) so that the holes of the inner tube are closed. A bright, luminous flame, rich in carbon, will result. A piece of porcelain held into it will become covered with soot. Now turn the collar so as to open the holes. The flame changes its character at once. The non-luminous blue color of burning carbon monoxide replaces the incandescent carbon, which had rendered the flame luminous. No soot will now be deposited on the porcelain. With this non-luminous, but very hot modification of the flame most operations of the laboratory are performed.

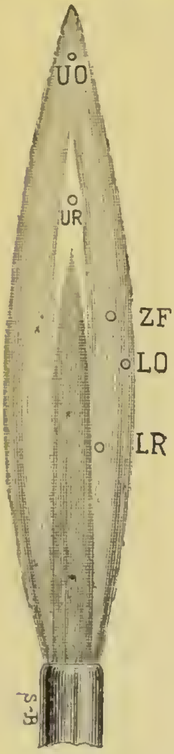


FIG. 2.

The following parts of the flame are distinguished. (fig. 2.)

A **dark cone** in the center, rising from the base, consisting of unburnt gas mixed with a considerable portion of air: the outer flame consists of burning carbon monoxide, in which different parts are distinguished.

The **zone of fusion** near the upper end of the dark cone, in which the temperature attains its highest degree half-way between the dark cone and the outer margin.

The **upper** and **lower oxidation** flames, which, being near the edge of the flame, are richest in oxygen and are the places in which oxidation occurs most readily, and are used for the oxidation of metals, etc.

The **upper** and **lower reduction** flame, **U.R.** and **L.R.,** being situated in the inner part of the flame, containing most carbon, are employed for reducing metallic oxides, etc.

The **upper reduction flame, U.R.,** is produced by partial shutting of the air-holes and forms a luminous tip of the dark cone.

The luminous flame is surrounded by a non-luminous margin or seam, called the **mantle,** in which more perfect combustion occurs by contact with the oxygen of the surrounding air. This mantle, though not so readily observed in the non-luminous flame, nevertheless forms, even there, a separate part of the flame and may be shown by coloration with boracic acid, or other substances, to be sharply differentiated from the inner part of the non-luminous flame, which lies between the mantle and the dark cone.

For blow-pipe operations and for the bending of glass tubes, flat jets of different size may be attached to the top of the burner, so as to give a thin, flat flame of such breadth as is most suitable to the work to be done.

Care must be taken that the flame do not flash back and burn at the end of the little jet. (A, fig. 1.) Heating of the lamp and spoiling of the rubber connections result from this; the flame at the top (E) has then a peculiar color and appearance, which at once reveals the accident. The lamp must in this case be extinguished and relighted.

Exercises. Hold a piece of **platinum foil** into the top of the **non-luminous** flame by means of a pair of tongs. Move it slowly up and down in the flame and mark the place of highest heat. Observe that it cannot be fused, that it is not tarnished, even at white heat. Put a drop of **distilled water** on it and hold it **over** the top of the flame. The water evaporates, leaving **no residue.** Next evaporate a drop of **ammonium chloride** solution over the top of the flame. It leaves a white residue, which volatilizes when heated to red heat. Evaporate a drop of solution of **magnesium sulphate;** a white residue remains, not volatilized at the highest heat of the flame.

Caution. Platinum, while heated, must never be brought in contact with fusible metals, sulphur or sulphides, chlorine, phosphorus or substances from which these may be set free during the heating operation. When soiled, the platinum must be promptly cleaned and burnished. If a stain clings to it obstinately, it may be removed by melting some borax or potassium bisulphate upon it.

Exercises. At the end of a **platinum wire** bend a round loop of about two millimetres (1/12 inch) in diameter. Light the Bunsen lamp (with the air-holes open) and tilt it into an oblique position, so that the salts, melted in the flame, cannot drop into the tube. Heat the loop of the platinum wire and plunge it into powdered **borax**. A portion of this will adhere to the loop, and when brought into the upper oxidation flame, will at first swell up and afterwards melt quietly into a transparent bead. Put now into a watch-glass a drop of **cobaltous nitrate** solution, dip the borax bead into it and then heat it again. The bead will assume a beautiful blue color. Next use a solution of **potassium dichromate** with a new borax bead; the color will be emerald green. With another bead use solution of copper sulphate, the color of the bead, while hot, will be bluish-green, becoming blue on cooling.

Repeat the same exercises with **microcosmic salt** instead of borax. Greater care must be taken to prevent the melted salt from dropping off the wire loop, which should be made a little less in diameter.

Beads, while hot, may by a quick jerk be thrown off of the platinum wire into a porcelain dish, and preserved for comparison.

To heat a liquid in a **testtube,** it is best to hold the tube by a narrow strip of folded paper, wrapped around it near the open end. The tube should be held slightly inclined into the current of hot air ascending above the flame and brought into the flame gradually and cautiously, while the liquid is gently shaken.

Larger quantities of liquid are heated in a glass flask, set upon the iron rings of the support, a piece of wire netting being placed beneath it for protection from direct contact with the flame. A porcelain dish is employed to evaporate liquids, care being taken to prevent the parts above the level of the liquid from getting overheated. Occasionally evaporation is done in a beaker-glass, in which case special precautions against fracture must be taken, by interposing wire netting or a sand bath between it and the flame. The moisture condensing on the outside of vessels containing cold liquids should be carefully wiped off. Water-baths, sand-baths and other devices serve to apply constant and regulated degrees of heat for a longer time.

Distillation. Volatile liquids are separated from less volatile liquids, or from solids, by distilling them from a retort or a glass flask, closed by a cork, through which a suitable glass tube passes, which conducts the vapor to the refrigerator, to be condensed into a liquid again. The refrigerator usually employed is the one known as Liebig's condensor. To this the receiver is adapted more or less closely according to the volatility of the distillate.

To prevent fracture of glass vessels by the bumping (succussion), occasioned by the tumultuous, intermittent boiling of some liquids, such as sulphuric acid, fragments of glass, or a small spiral of platinum wire are placed into the vessel.

2. USE OF THE BLOWPIPE.

The blowpipe serves to direct a very intense flame upon a limited space. Any of the various modifications may be used after a little practice. To use it, the mouth is filled with air, which is forced into the tube by pressure from the cheeks alone, not by blowing from the lungs, and is replenished from time to time without interrupting the blowing, the respiration being carried on through the nose.

A large candle, an oil lamp with flat wick, or the luminous flame of the Bunsen lamp (especially when produced by a special flat blowpipe burner) may be used with best advantage for the **reducing** operations, while, for **oxidation,** an alcohol flame or the non-luminous gas flame are preferable. By the current of air from the blowpipe the flame is blown sideways and slightly downward, and is rendered long and narrow. It is supplied with an extra supply of oxygen so as to produce a more intense combustion of its carbonaceous particles. The outer part of the flame, containing the largest supply of oxygen is used for oxidizing metals, etc., while the part nearest to the base of the flame, having more carbonaceous matter, yet unburnt, serves for reduction of oxides. The operator may, at will, produce a flame in which either the **oxidizing** or the **reducing** influence is intensified, accompanied with a high heat. To produce a strong reducing flame, a large flame is selected (the gas turned on more freely) and the jet of the blowpipe held just outside the flame, a little above its base, while a moderate current of air serves to tilt the flame, without depriving it of the luminous appearance, indicating the presence of incandescent carbon.

A lesser flame suits best for **oxidizing.** The jet of the blowpipe is then held a little inside of the flame, and a stronger current passed so as to supply oxygen enough for complete combustion of the carbon. The flame becomes non-luminous, its point of highest heat is at the apex of the inner cone, and substances, to be oxidized, are held a little beyond this point.

To support substances in the flame we generally use charcoal, made of pine or other soft wood, for reduction experiments, and platinum wire or foil for oxidation. Many operations, formerly effected in the blowpipe flame, are now more conveniently performed in the flame of the Bunsen gas lamp.

Exercises. Select a smooth piece of charcoal, about 70 millimetres long, 40 Mm. broad and 20 Mm. in thickness; near the corner, that will be held nearest to the flame, scoop out a small, shallow cavity. Into this place a very small crystal of **potassium nitrate** and direct the point of the blowpipe flame upon it. At first it will melt, then excite a vivid combustion of the heated charcoal, accompanied with coruscations. (We call this appearance deflagration, and recognize by means of it substances very rich in oxygen, such as nitrates or chlorates.) As soon as this begins, the blowpipe must be withdrawn. and care be taken to guard against the hot particles flying about.

Upon another portion of the charcoal place a small quantity (not larger than a garden pea) of **litharge.** Direct upon it a full sized, reducing flame, so that it impinges upon the charcoal just in front of it, and then spreads over it. The lead oxide will melt, lose its oxygen, and a globule of metallic lead will result, surrounded by an incrustation of volatilized oxide.

Upon another portion of charcoal place a small piece of crystallized **alum.** In the oxidizing flame it will melt and lose its water. Put upon it now a drop of the solution of cobaltous nitrate and heat again. An opaque blue mass will result.

Repeat the last experiment with **zinc sulphate** instead of alum. On reheating after receiving the drop of cobalt solution, it will become bright green.

3. MANIPULATION OF GLASS-TUBING.

Tubing of easily fusible soda-glass, free from lead, from 4 to 5 Mm. in diameter, and of moderate thickness of wall, is most suitable for experimenting.

Cutting off. A small incision is made, with a triangular file, at right angles to the axis of the tube. The tube is held in both hands, with the thumbs opposite to the cut of the file, and the piece is separated more by pulling than by bending. Very thin glasstubes, or those of larger diameter, such as a test tube cannot be easily cut in this manner. An incision with a file is made as above, and a piece of highly heated solid glassrod is then held in the direction of the cut, a little in advance of it. The cut will crack and by guiding the hot rod just ahead of the end of the crack, this may be led accurately around the tube.

Smoothing ends. The sharp edges of cut glass tubing must be rounded by holding them into the edge of the flame, until melted, while the tube is rotated to insure an equal heat. If held into the flame too long the opening narrows, the margin thickens and finally the tube closes up entirely. A platinum wire, inserted into the end before it is fully closed, may thus be firmly fixed into the glass tube which then serves as a handle. The closing operation is most easily done before the blowpipe.

Drawing out to a point. To make a pipette or a jet for a hydrogen apparatus, a sufficient length of tube is held by both ends, so as to place the part, where the point is to be, horizontally into the hotter, upper part of the flame, and is there continually rotated on its axis. As soon as it softens sufficiently, (which is accompanied by the yellow coloring of the flame, from the volatilization of the soda of the glass) it is taken out of the flame and drawn out in the direction of its axis. If a small part only was heated, and a quick pull made, the points will be blunt, if otherwise, of a longer, gradual taper; a very thin tube connects the two points. The tube is cut off at the point, as before directed, so as to have an orifice slightly larger than desired, and the end finished smooth by melting the margins in the edge of the flame.

If it is desired to **close the end** of the tube, a very short portion is heated in the point of the flame and the end quickly drawn off and rounded by rotating it for some time in the flame.

Blowing a bulb. This is done by heating the closed end of a tube in the hottest part of the flame and, after removing it out of the flame, blowing steadily into the open end, until the necessary size is obtained. Careful rotation in the flame is necessary to form a symmetric bulb.

Bending. This must be done so as to preserve an even calibre of the tube throughout the bend. To succeed a sufficiently long piece of tube must be heated simultaneously, and equally on all sides. Hence the flat burner attached to the Bunsen lamp, or the ordinary fishtail gas burner, or a flat wick oil-lamp will give the best flame for the purpose. If we use the ordinary Bunsen burner, the tube must be held obliquely, so as to heat a longer piece. Continual rotation, while in the flame, is necessary to insure an equal heating of all sides. The softening must not be carried too far, and the proper shape should be given, after removal out of the flame, by a steady, continuous bending of the tube at a single operation. Before a tube is bent, its ends should receive such finish as they require, either be rounded off, or pointed, or closed, as after the bending rotation in the flame is interfered with, and a good finish can only be made with difficulty.

4. WORKING WITH CORKS.

Corks should be selected of a soft, uniform texture, as free as possible from cracks or holes. To fit them air tight to bottles or flasks, they must be chosen somewhat larger than the mouth of the bottle, soaked for some time in warm water, and compressed while wet and soft, so as to make an accurate fit. If they are liable to come in contact with corrosive liquids or gases, they may be dipped into melted paraffin.

To perforate corks for the insertion of glass-tubing, cork borers, containing various gradations in size, are frequently used, but the object may be very well accomplished by a round file with long gradual taper, usually called a rattail file. The size of the file or borer is so selected as to be somewhat smaller than the tube. Marks are made on both ends of the cork, and the perforator is then inserted so as to be at right angles with the surface of the cork. The boring from one side is carried about half way through, and the hole finished from the opposite side. Even with the best cork borers this is preferable to use from one side but, whenever the latter method is chosen, the end of the cork opposite the borer must be supported against a piece of wood, to prevent the breaking out of an irregular piece at the end of the hole. It is then carefully smoothed with the file and must be very slightly less in size than the glass tube, so that this will require some force to insert it. Care must be taken to prevent breaking the tube, by pressing it in gently and with rotation. It must fit air-tight without lutes or cements.

When a smaller cork is to be cut out of a larger piece, a very sharp and broad bladed knife should be used, to insure a smooth surface. The knife should be rather drawn than pressed in making the cut. Soaking in warm water somewhat facilitates the smooth trimming of cork.

5. FILTRATION.

When liquids are to be separated from solid particles suspended in them, they may be permitted to stand until the precipitate has collected at the bottom, and then the clear liquid carefully poured off. This process is called **decantation.** A more thorough separation is effected by **filtration.** In this case the liquid containing the precipitate is poured upon a filter, made of specially prepared paper, supported in a glass funnel. The funnel should have sides meeting at an angle of 60 degrees, and a shank properly proportioned in width. For analytical purposes funnels of 50 to 70 millimeters in diameter, are the most useful. The filters are cut from square paper of double the diameter of the funnel by folding it through the center, into halves, then into quarters and eighths. This folded paper is then laid into the funnel so that its apex reaches a little above that of the funnel, and the base is pressed against the rim of the funnel, sufficiently, to mark its round contour upon the paper, it is then taken out and cut along the marked line and opened so as to lay folded in quarters. When filter paper is furnished already cut in circular pieces, the folding is only done twice, so as to form quarters. The filter is then opened so as to leave three thicknesses of paper on one side, and one on the other. It is now placed into the funnel, and should fit closely to the sides and not quite reach to the upper rim. It is then slightly moistened with distilled water, and is ready to receive the liquid to be filtered. This plain and close fitting filter is always employed when the precipitated solid as well as the liquid filtrate are to be obtained separately for examination.

Much more rarely a plaited filter is used to filter quickly larger quantities of turbid solutions. This is constructed by repeating the folding until 16 or 32 sectors are formed, and these are opened out and placed into the funnel, so as to form a zigzag line at the rim. The funnel with its contents is supported on the ring of a filtering stand and the receiving vessel, either a beaker glass or a flask, so placed that the shank of the funnel may touch the inner wall of the receiver a little below its upper edge. The filtrate will, by these means, flow quietly down the side without waste. The filter is never to be filled to its rim. If the paper be thin or solutions are to be filtered under pressure, double filters and short cones of stout parchment paper, or of platinum foil are sometimes needed to prevent the liquid from breaking through.

The transfer of liquid to the filter must be done carefully to prevent waste by spilling. A glass stirring rod held to the rim of the beaker, inclined for pouring out, so that its end is placed over the filter, will cause the liquid to flow along its length and drop off at the end. Care must be taken to prevent the liquid remaining in the beaker, after filling the filter, from flowing down the outer side of the beaker; this may be done by turning the part, where, after pouring out, the last drop still adheres, quickly to such a position that it forms the highest point, from which the drop must flow the inner side again.

Many substances pass but slowly through the filter and various devices are resorted to to accelerate the tedious process. The Bunsen water-air-pump or various aspirators are employed to exhaust the receiving vessel, into which the funnel fits air-tight, so as to let the pressure of the atmosphere force the liquid rapidly through the filter, which must be reinforced at the apex by a short cone of platinum foil or parchment paper as above mentioned. A very simple but efficient device for the same purpose is the pig-tail attachment to the funnel, as represented in figure 3. A tube (DE) bent upon itself at (C) is joined to the funnel (A) by the rubber connector (B), and if greater pressure is desired a long tube may be attached to its lower end (E). The circular bend (C) occasions the coherence of the liquid flowing from the filter in a continuous column, whose weight exhausts the space below the filter, and lets the atmospheric pressure force the liquid through more rapidly. With a long tube the end of the filter must be reinforced by a cone of parchment paper (P).

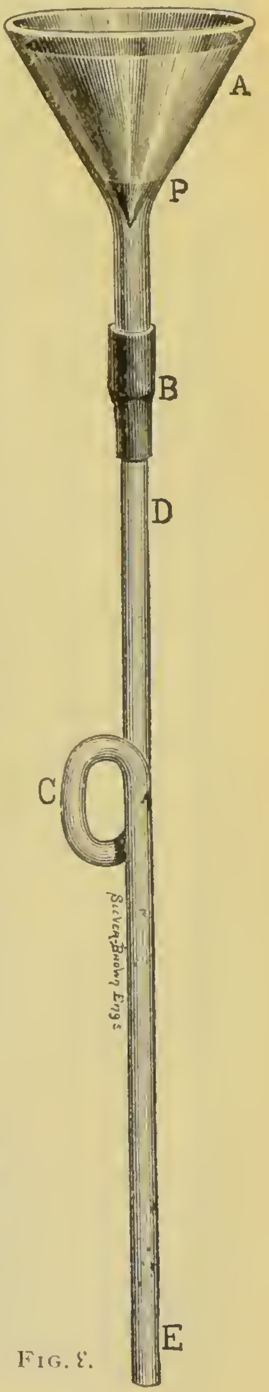


FIG. 3.

Many precipitates require washing out on the filter to free them from the last traces of the liquid in which they were suspended. This may be done by the wash-bottle (or spritz flask) by directing its stream against the upper part of the filter, so as to collect into the bottom part all of the solid particles.

When gelatinous precipitates, such as ferric hydrate, or alumina, are to be washed, special care must be taken to let the washing be continuous, lest the mass get dry, and contract so as to form fissures through which the wash-water flows rapidly without penetrating the whole mass.

6. MISCELLANEOUS NOTES.

THE utmost care is required to use perfectly clean vessels for all the operations of analysis. Testtubes should be rinsed with water as soon as possible after having been used and, if necessary, cleaned with the testtube brush. A final rinsing with rain or distilled water becomes necessary when the ordinary water is too impure. When not in use, they should be kept on the upright pegs of the stand with the open end downward to prevent accumulation of dust in them. All other glass vessels should be similarly cleansed. When solutions of standard strength are to be transferred into burettes, reagent bottles, or other vessels, the last rinsing must be with a small portion of the standard solution, which they are to contain. Drying of glasstubes, preparatory to heating solids in them, is done by holding them over the flame, while the air is drawn out of them by the mouth through a small glass tube reaching near to their bottom.

Reagent bottles containing caustic alkalies or their carbonates are liable to have their glass stoppers corroded and so firmly fixed, that they are very troublesome to open. It is best to prevent this by dipping the stoppers into melted paraffin, which is not affected by the reagents, lubricates the stopper perfectly and gives an air-tight closure.

In order to render soluble some solid substances, such as insoluble silicates, sulphates or aluminum compounds, it is necessary to flux them. For this operation they are converted into very fine powder, by crushing in a steel mortar (sometimes called diamond mortar), triturating them very carefully in a small agate mortar, and sifting out the finest powder. This powder is then mixed with the flux, which generally consists of sodium carbonate or bi-sulphate and placed on a piece of platinum foil, or, if larger quantities are to be operated on, in a crucible of platinum and heated by a burner producing very high temperature, until the whole mass is uniformely melted. When arsenic, antimony, bismuth, tin, lead, or other easily reducible metals are contained in the insoluble solid to be fluxed, platinum crucibles would be injured, and instead thereof, porcelain crucibles should be used.

It will facilitate work greatly if the reagent bottles are always kept on the shelves, in a certain definite order, and every one returned at once to its place, before another is taken down. This insures the ready finding of every reagent, and prevents the exchange of glass stoppers by which reagents are mixed and rendered impure, and errors are easily committed.

The amount of specimens taken for the various operations described in the following **examples for practice** is generally small. Thus for dry substances to be tested in the ignition tube (a small tube of hard glass, closed at one end), a portion of the size of a small pea will suffice. For making solutions somewhat more is generally required, according to the number of tests to be made with the solution. Solutions, if not otherwise directed, should be nearly saturated and for each individual reaction about four cubic centimetres (a teaspoonful) should be poured into the test tube. When reagents are directed to be added in **excess,** it is not intended that very large quantities be used, but only that somewhat more be added than enough to produce the neutralization, or precipitation of the substance operated on.

In some cases a reagent produces a precipitate when added in an equivalent quantity, but the least excess begins to re-dissolve the precipitate, and an equal equivalent quantity is requisite to complete the re-solution. This is somewhat inaccurately expressed: a precipitate is formed by a reagent, soluble in excess.

EXAMPLES FOR PRACTICE IN QUALITATIVE ANALYSIS.

I. SODIUM CHLORIDE. NaCl.

Common Salt.

1. When **sodium chloride** is heated in a small tube of hard glass, closed at one end, it will decrepitate and, at a higher heat, will melt.

a. REACTIONS FOR SODIUM.

2. A small particle of sodium chloride is attached to the loop of a platinum wire, and introduced into the outer margin of the Bunsen gasflame or into the oxidation flame of the blowpipe, or the alcohol flame. The flame is thereby colored intensely **yellow.** A crystal of red **potassium bichromate, $K_2Cr_2O_7$,** illuminated by this yellow flame, so as to either transmit or reflect its light, appears colorless: paper coated with red **mercuric iodide, HgI_2,** appears white. The yellow color of the flame disappears when viewed through blue cobalt glass or a solution of indigo: when viewed through the spectroscope the flame shows a yellow line.

Sodium chloride, **NaCl,** dissolves easily in water. The solution is neutral to test-papers. In this solution the presence of **chlorine, Cl,** is shown by the following:

b. REACTIONS FOR CHLORINE.

3. **Silver Nitrate, $AgNO_3$,** produces a white, curdy precipitate of **silver chloride, AgCl,** soluble in **ammonium hydrate, $NH_4.OH$,** insoluble in **nitric acid, HNO_3.** The ammoniacal solution of **AgCl** is therefore reprecipitated by acidulating with **HNO_3.** The precipitate darkens when exposed to sun-light.

4. **Mercurous nitrate, $Hg_2(NO_3)_2$:** white precipitate of **calomel (mercurous chloride), Hg_2Cl_2,** insoluble in **HNO_3**; blackens upon addition of **$NH_4.OH$. $Hg_2Cl_2+2(NH_4.OH)=N_2Hg_2H_6.Cl_2+2H_2O$].**

5. **Lead acetate, $Pb(C_2H_3O_2)_2$:** white crystalline precipitate of **lead chloride, $PbCl_2$,** insoluble in **NH_4OH,** soluble in 33 parts of boiling water, from which, on cooling, it separates in crystalline needles.

6. Concentrated **sulphuric acid, H_2SO_4,** poured upon **NaCl,** causes effervescence with evolution of pungent vapors of **hydrochloric acid, HCl.** The vapors have an acid reaction, they turn moist **blue litmus** paper **red,** or **reddened phenol phthaleine** paper **white,** or **browned turmeric** paper **yellow.** A glass-rod dipped into ammonia water and held at the mouth of the tube will be surrounded by dense white fumes of **ammonium chloride, NH_4Cl.**

II. SODIUM CARBONATE, $Na_2CO_3+10H_2O$.

Sal Soda.

a. REACTION FOR WATER.

1. When heated in a glasstube, water is given off and deposits itself in small drops on the cooler portion of the tube.

b. REACTION FOR SODIUM.

2- The flame is colored yellow, thus showing presence of **Na.** (See I. 2.)

3. Soluble in water. The solution has **alkaline** reaction, *i. e.* it changes the color of **red litmus** paper to **blue,** and that of **white phenol-phthaleine** paper to **red,** and **yellow turmeric** paper to **brown.**

c. REACTION FOR CARBONIC ACID GAS.

4. On addition of **hydrochloric acid, HCl,** it effervesces, giving off a colorless gas, **carbon di-oxide, CO_2,** otherwise called **carbonic acid gas.** This gas is so heavy that it may be poured out of the testtube, (care being taken that none of the liquid is poured out with it) into another testtube containing some clear **lime water, $Ca(OH)_2$.** The **CO_2** gas renders the clear lime water turbid by the production of white, insoluble **calcium carbonate, $CaCO_3$.**

III. SODIUM SULPHATE. $Na_2SO_4+10H_2O$.

Glaubers Salt.

a. REACTION FOR WATER.

1. On heating in glasstube water, H_2O, is given off.

b. REACTION FOR SODIUM.

2. The flame is colored yellow.

c. REACTIONS FOR SULPHURIC ACID.

3. When sodium sulphate is heated on charcoal, in the reduction flame of the blow-pipe until the fused mass becomes brown, **sodium sulphide, Na_2S,(Hepar),** is formed by the withdrawal of oxygen. The fused mass is detached from the charcoal, placed upon a bright silver coin and moistened by a drop or two of water. A black stain of **silver sulphide, Ag_2S,** is produced.

Dissolve the sodium sulphate in water and add as follows:

4. **Barium chloride, $BaCl_2$:** white precipitate of **barium sulphate, $BaSO_4$,** insoluble in acids.

5. **Lead acetate, $Pb(C_2H_3O_2)_2$:** white precipitate of **lead sulphate, $PbSO_4$,** insoluble in dilute acids. On addition of **hydrogen sulphide, H_2S,** the precipitate turns black. **$PbSO_4+H_2S=H_2SO_4+PbS$.**

IV. POTASSIUM NITRATE. KNO_3.

Saltpetre.

1. When heated in the glass-tube saltpetre melts and, at higher heat evolves oxygen, leaving a residue of **potassium nitrite, KNO_2.**

2. On heating saltpetre on charcoal before the blow-pipe, it deflagrates, leaving a residue of **potassium carbonate, K_2CO_3.**

a. REACTIONS FOR POTASSIUM.

3. The flame is colored **violet.** When viewed through **blue glass** or **indigo solution** it appears intensely red, even when the glass or indigo solution is doubled in thickness. The spectroscope shows characteristic lines. (see table.)

A **saturated solution** in water gives the following reactions:

4. **Sodium acid tartrate, $NaHC_4H_4O_6$** produces a white crystalline precipitate of **cream of tartar (potassium acid tartrate,) $KH.C_4H_4O_6$.** In diluter solutions this precipitate forms

but slowly: shaking the testtube, rubbing its inside with a glass rod, or addition of alcohol accelerates its separation. In very dilute solutions no cream of tartar precipitates, as it is soluble in 210 parts of water.

5. **Platinic chloride ($Pt\,Cl_4$)** produces a **yellow** precipitate of **$PtCl_4.2KCl$.** **$3PtCl_4 + 4KNO_3 = 2PtCl_4.2KCl + Pt(NO_3)_4$.** In dilute solutions the precipitate falls slowly; more quickly after addition of alcohol.

6. **Hydro-fluo-silicic acid, H_2SiF_6,** produces a transparent colorless precipitate of **potassium silico-fluoride, K_2SiF_6.**

$2KNO_3 + H_2SiF_6 = K_2SiF_6 + 2HNO_3$.

The precipitates 4, 5 and 6 are not produced in *very dilute* solutions on account of their solubility in much water, hence dilute solutions of potassium salts must be concentrated by evaporation in a porcelain dish before the reagents are applied.

7. **Sodio-cobaltic nitrite,*** **($6NaNO_2.Co_2(NO_2)_6$,** added to the potassium solution gives a yellow precipitate of **potassio-cobaltic nitrite, $6KNO_2.Co_2(NO_2)_6$.** The addition of a few drops of **acetic acid, $HC_2H_3O_2$,** hastens the reaction, which occurs even in great dilutions, especially if the reagent contains an excess of **$NaNO_2$.**

b. REACTIONS FOR NITRIC ACID.

8. To the solution of **KNO_3** an equal volume of concentrated **H_2SO_4** is added and the testtube set aside to cool. In another testtube a fresh crystal of **ferrous sulphate, $FeSO_4$,** is dissolved in a little water and this solution poured cautiously on top of the cooled mixture in the first tube. A brown ring will mark the line of contact, (**$2FeSO_4.NO$**). Heat quickly disperses the ring by the formation of ferric sulphate and the expulsion of nitric oxide.

9. To the solution of **KNO_3** add a little solution of **indigo** and **HCl.** Boil and the blue color will be replaced by yellow. **$3C_8H_5NO$(Indigo) $+ 2HNO_3 = 3C_8H_5NO_2$(Isatin,** orange) **$+2NO + H_2O$.**

10. A dry mixture of **KNO_3** and copper chips is heated with

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* Sodio-cobaltic nitrite solution may be prepared by dissolving in sufficient water, separately, 10 grammes pure sodium nitrite and 4 grammes cobaltous nitrate, mixing the solutions, adding 2 cubic centimeters of acetic acid and filling up with water to make 100 C.C. The presence of Ba, Sr, Ca, Mg, and Zn, does not interfere with its action on K. Ammonium, rubidium and caesium form with it precipitates similar to potassium.

concentrated H_2SO_4. **Brownish-red** vapors of NO_2 escape.

11. To the solution of **KNO_3** add **sodium hydrate** and, either **aluminium**, or **zinc** and **iron** in filings or small chips. On heating, **ammonia, NH_3**, is given off.

$$KNO_3 + 8H = NH_3 + KOH + 2H_2O.$$

V. AMMONIUM CHLORIDE. NH_4Cl.

Sal ammoniac.

1. When heated in a glass tube, or upon charcoal, **ammonium chloride, NH_4Cl**, sublimes without melting.

a. AMMONIUM REACTIONS.

2. In a saturated aqueous solution **$PtCl_4$** produces a **yellow** crystalline precipitate of **$PtCl_4 . 2NH_4Cl$**.

3. **Sodium acid tartrate, $NaH.C_4H_4O_6$**: white crystalline precipitate of **ammonium acid tartrate $NH_4H.C_4H_4O_6$**, soluble in much water and in **$NH_4.OH$**.

4. To the solution of **sal ammoniac** add **sodium hydrate, $NaOH$**, and heat slightly. **Ammonia gas, NH_3**, is given off, recognizable by its **odor**. The gas shows **alkaline** reaction with **moist** testpapers held **above** the liquid. **Red litmus** paper turns **blue, yellow turmeric** paper **brown, white phenol-phthaleine** paper becomes **red** in the vapor. A glass rod dipped into dilute **HCl** or into **acetic acid, $H.C_2H_3O_2$**, shows dense white fumes, when held into the vapor. A small beaker glass or a porcelain dish is better suited for these reactions than a testtube.

5. **Sodio-cobaltic nitrite, $6NaNO_2.Co_2(NO_2)_6$**, produces in concentrated solutions of **NH_4Cl** a **yellow** precipitate of **$6[NH_4.NO_2]Co_2(NO_2)_6$**.

6. Traces of **$NH_4.OH$** (in drinking water) are detected by **Nesslers reagent** (a solution of **HgI_2** in **KI**, made strongly alkaline by **KOH**) a reddish brown precipitate or coloration is produced when an ammonia salt is present. **$2(HgI_2.2KI) + 3KOH + NH_4OH = (NH_2.Hg.I)HgO + 7KI + 3H_2O$**. Excess of **KI** redissolves the precipitate, hence the reagent must be preserved with an excess of **$Hg I_2$** in the bottle.

7. **Hydro-fluo-silicic acid, H_2SiF_6**, gives no precipitate.

b. CHLORINE REACTION.

8. **$AgNO_3$** gives a white precipitate of **AgCl**; (see I, 3).

VI. POTASSIUM AND SODIUM TARTRATE.

$KNaC_4H_4O_6+4H_2O$.

Rochelle Salt.

1. Heated in glass tube it gives off water.

a. REACTIONS OF TARTARIC ACID.

2. Heat a small portion on platinum foil; it melts, then blackens, giving off vapors, whose smell resembles that of burnt sugar.

3. The charred residue is transferred to a testtube, water is added, and, after slight heating, the black mixture is filtered. Charcoal remains on the filter, the solution contains **carbonates,** which show alkaline reaction with testpapers and effervesce on adding **HCl.**

4. To a saturated solution of the salt add some **acetic acid,** $H.C_2H_3O_2$: a precipitate of **cream of tartar,** $KHC_4H_4O_6$, will fall.

b. REACTIONS OF BASES.

5. Dip the loop of a clean platinum wire into the liquid obtained by filtering the charred residue and treating with **HCl** (3). It will color the flame yellow, showing the presence of **Na**; now view the flame through blue glass: the yellow rays will be quenched and a red color remain, indicating **K**.

6. For other reactions of **K** compare IV. 3 and following.

VII VIII. SODIUM PHOSPHATE. $Na_2HPO_4+12H_2O$.

1. Heat in glass tube—water.

2. Heating on platinum foil to red heat, converts it into **sodium pyrophosphate,** $Na_4P_2O_7$. $2Na_2HPO_4=Na_4P_2O_7+H_2O$. The yellow flame shows presence of sodium.

3. The aqueous solution reacts alkaline.

REACTIONS OF PHOSPHORIC ACID.

4. In the solution of **sodium phosphate,** Na_2HPO_4, (ortho phosphate) $AgNO_3$ produces a **yellow** precipitate of Ag_3PO_4, soluble in $NH_4.OH$ and in HNO_3. In a solution of the **pyrophosphate,** made from the residue on the platinum foil (2), $AgNO_3$ precipitates **white pyrophosphate of silver,** $Ag_4P_2O_7$.

5. $Pb(C_2H_3O_2)_2$: white precipitate, $Pb_3(PO_4)_2$ soluble in HNO_3.

6. **$CaCl_2$** or **$BaCl_2$**: white precipitate of **$CaHPO_4$** or **$BaHPO_4$** soluble in **HCl**. If to this solution in **HCl ammonium hydrate** is added, a precipitate falls having the constitution **$Ca_3(PO_4)_2$** or **$Ba_3(PO_4)_2$**.

$3CaHPO_4+3NH_4.OH=Ca_3(PO_4)_2+(NH_4)_3PO_4+3H_2O$.

7. To the solution of **Na_2HPO_4** add **NH_4Cl, $NH_4.OH$** and **magnesium sulphate, $MgSO_4$**. A white crystalline precipitate, **$Mg(NH_4)PO_4$**, falls, insoluble in **$NH_4.OH$**, soluble in acids.

8. To a small quantity of solution of **Na_2HPO_4** add **ammonium molybdate solution in HNO_3, $(NH_4)_2MoO_4$**, in excess (about 5 times the quantity of the phosphate solution). A bright yellow precipitate of **ammonium phospho-molybdate, $(NH_4)_3PO_4+10MoO_3$**, is produced. This is insoluble in **HNO_3**, soluble in **$NH_4.OH$** and in **phosphoric acid, H_3PO_4**. From the ammoniacal solution the **$Mg(NH_4)PO_4$** is precipitated by the addition of **NH_4Cl** and **$MgSO_4$**.

VIII. SODIUM DIBORATE. $Na_2B_4O_7+10H_2O$.

Borax.

1. Heated on the loop of a platinum wire borax swells up at first, loses its water of crystalization, and finally melts into a transparent colorless bead. The yellow flame shows **Na**.

2. The aqueous solution shows feeble alkaline reaction.

REACTIONS OF BORACIC ACID.

3. To a hot saturated solution of borax add some **concentrated H_2SO_4**. On cooling **boracic acid, $B(OH)_3$** will separate in shining scales.

4. **$CaCl_2$** or **$BaCl_2$** produce in concentrated solution of borax white precipitates of **calcium diborate, CaB_4O_7**, or **Barium diborate, BaB_4O_7**, soluble in much water.

5. Into solution of borax, acidulated with **HCl**, a strip of **turmeric** paper is dipped. The paper, after drying, has a **reddish brown** color, similar to that produced by alkalies.

6. In a porcelain dish some borax is mixed with **H_2SO_4**. On this a little alcohol is poured and ignited. The flame has a seam or mantle of a green color, which shows best when it is repeatedly extinguished and rekindled. (As the sodium sulphate, produced by addition of sulphuric acid, is insoluble in alcohol, the sodium cannot color the flame, and only the boracic acid

communicates its green color to it.) Another mode of showing the green flame of boracic acid, without permitting the sodium flame to hide it, is to mix a little borax with H_2SO_4, dipping the loop of the platinum wire into it and holding it **just outside the lower portion** of the Bunsen gas flame, not allowing it to touch the flame. The boracic acid volatilizes and its vapor colors the mantle of the flame green, while the sodium does not affect it. The same result may be partially effected by mixing the borax with **glycerine** and introducing the paste into the flame.

As there are several other substances producing a green flame, such as phosphates, coppersalts etc., the spectroscope will best indicate the difference.

IX. MAGNESIUM SULPHATE, $MgSO_4+7H_2O$.

Epsom Salt.

1. Heated in glass tube: water.

a. MAGNESIUM REACTIONS.

2. From the aqueous solution **NaOH**, or **$NH_4.OH$** precipitates **magnesium hydrate, $Mg(OH)_2$,** soluble in **NH_4Cl**.

3. **Sodium carbonate, Na_2CO_3** precipitates **white, basic magnesium carbonate, $4MgCo_3.Mg(OH)_2$,** soluble in **NH_4Cl.**

4. **Neutral ammonium carbonate,** $(NH_4)_2CO_3$ in excess (made by adding **NH_4OH** to the solution of the ordinary ammonium carbonate, which consists of a mixture of dicarbonate with carbonate,) produces in concentrated solution of **$MgSO_4$** a precipitate of **$MgCO_3.(NH_4)_2CO_3$,** insoluble in excess of ammonium carbonate.

5. Ordinary **ammonium carbonate** containing **dicarbonate,** does not immediately nor perfectly precipitate magnesium salts. If **NH_4Cl** be added, no precipitate occurs. If now **Na_2HPO_4** be added, a white precipitate of **magnesium ammonium phosphate, $Mg(NH_4)PO_4$,** falls, (see VII. 7) insoluble in **NH_4OH,** soluble in acids.

b. REACTIONS OF SULPHURIC ACID.

6. Heat some **epsom salt.** mixed with dry **sodium carbonate,** upon charcoal, in the reduction flame of the blow pipe. **Hepar** is formed (see III. 3. and ff.)

X. CALCIUM CARBONATE, $CaCO_3$.

Marble, Chalk.

1. No change by heating in glass tube.

2. When heated on charcoal, before the blow pipe, CO_2 escapes. The residue reacts alkaline on moist test papers.

3. Insoluble in water. Boil a small piece of marble with distilled water. Place a drop of this on platinum foil and evaporate over the flame. No residue will remain.

a. REACTIONS OF CARBONIC ACID.

4. Place a small piece of marble into a testtube, add **HCl**: there will be effervescence and if the gas is decanted into a test-tube containing some **clear lime** or **baryta-water,** it will render them turbid. (see II. 4.) Or else if a glass tube, having a drop of clear barytawater hanging to its end, be held into the test-tube, in which the effervescence takes place, just over the liquid, the drop will become turbid from the formation of **$BaCO_3$.**

5. After the effervescence produced by **HCl** on marble has ceased and while an excess of marble is still in the tube, the liquid is heated to expel **CO_2** and then filtered. It now contains **calcium chloride, $CaCl_2$,** this is employed for making the following:

b. REACTIONS OF CALCIUM.

6. **NaOH** precipitates white **calcium hydrate $Ca(OH)_2$** soluble in about 700 parts of cold water.

7. **$NH_4.OH$** gives no precipitate.

8. **Na_2CO_3** or **$(NH_4)_2CO_3$** precipitates white **$CaCO_3$.**

9. **Na_2HPO_4** precipitates white **$CaHPO_4$** (see VII.6.), soluble in **acetic acid, $H.C_2H_3O_2$,** and in all mineral acids.

10. **Ammonium oxalate, $(NH_4)_2C_2O_4$,** precipitates white **calcium oxalate, CaC_2O_4,** insoluble in **$H.C_2H_3O_2$.** Soluble in **HCl** and in **HNO_3.** From these solutions it is again precipitated by **$NH_4.OH$.**

11. **H_2SO_4** produces white precipitate of **calcium sulphate, $CaSO_4$,** in concentrated solutions only, soluble in 500 parts of cold water and in **HCl.** Alcohol precipitates it from these solutions.

12. The flame is colored orange red by **$CaCl_2$** and gives a peculiar spectrum, easily recognized, (see table.)

13. No precipitate is produced by **potassium dichromate, $K_2Cr_2O_7$**, or by **hydro-fluo-silicic acid, H_2SiF_6.**

XI. BARIUM CHLORIDE, $BaCl_2+2H_2O$.

1. Heated in glass tube it yields **H_2O.**

2. Upon charcoal, before the blowpipe it melts and leaves a residue showing alkaline reaction on moist testpapers.

a. REACTIONS OF BARIUM.

3. **$BaCl_2$** colors the flame greenish yellow, giving a spectrum of many lines (see table).

4. **$BaCl_2$** dissolves readily in water.

5. From the aqueous solution **$NaOH$** precipitates white **$Ba(OH)_2$** soluble in 20 parts of cold and in 2 parts of boiling water.

6. **NH_4OH** yields no precipitate.

7. **Na_2CO_3** or **$(NH_4)_2CO_3$** precipitate white **barium carbonate, $BaCO_3$.**

8. **H_2SO_4** (or any **soluble sulphate**) precipitates white **barium sulphate, $BaSO_4$**, insoluble in all acids.

9. Hence **solution of gypsum (calcium sulphate, $CaSO_4$)** at once renders turbid a solution of a barium salt, forming **$BaSO_4$**.

10. **Na_2HPO_4** precipitates white **barium phosphate, $BaHPO_4$**, soluble in **HCl** (see VII. 6.).

11. **Hydro-fluo-silicic acid, H_2SiF_6**, produces a white precipitate of **$BaSiF_6$, barium silico-fluoride**, soluble in acids.

12. **Red potassium dichromate, $K_2Cr_2O_7$**, as well as **yellow potassium chromate, K_2CrO_4**, produces a yellow precipitate of **barium chromate, $BaCrO_4$**, insoluble in acetic acid, soluble in **HCl**, from which solution it is reprecipitated by **$NH_4.OH$.**

$$K_2CrO_4+BaCl_2=BaCrO_4+2KCl.$$

For reactions of chlorine, (see I. 3. etc.)

XII. STRONTIUM CHLORIDE, $SrCl_2+6H_2O$.

1. Water is given off on heating in glass tube.

2. When heated on charcoal before the blow pipe it melts and leaves a residue showing alkaline reactions.

REACTIONS OF STRONTIUM.

3. The flame is colored carmine red and gives a spectrum by which **Sr** is easily distinguished from the similar color given by **lithium.**.

4. The reactions produced by **$NaOH$, $NH_4.OH$, Na_2CO_3, $(NH_4)_2CO_3$** and **Na_2HPO_4** in an aqueous solution of a **strontium salt** closely resemble those of barium. (See XI. 5. 6. 7. 10.)

5. **H_2SO_4** precipitates **white strontium sulphate, $SrSO_4$,** insoluble in acids.

6. **$CaSO_4$** produces a turbidity **after some delay.**

7. **H_2SiF_6**: no precipitate.

8. No precipitate is produced by **red potassium dichromate, $K_2Cr_2O_7$,** in **neutral** or **acid** solutions of strontium salts. But **yellow potassium chromate, K_2CrO_4** slowly precipitates **Sr** from **neutral** solutions as **$SrCrO_4$,** soluble in acetic and other acids, and reprecipitated by **KOH**. If to a solution of **$SrCl_2$ $K_2Cr_2O_7$** be first added and then to the clear solution **KOH** until the reaction becomes alkaline, the same precipitate, **$SrCrO_4$,** is produced.

For reactions of chlorine see I.

XIII. CALCIUM SULPHATE, $CaSO_4+2H_2O$.

Gypsum.

1. On heating in glass tube water is given off.

a. SULPHURIC ACID REACTIONS.

2. When mixed with dry **Na_2CO_3** and heated upon charcoal in the reduction flame, hepar is formed. (Compare III. 3. 4. 5.)

3. **$BaCl_2$**: white precipitate of **$BaSO_4$**.

b. REACTIONS OF CALCIUM.

See calcium carbonate X., to which may be added the following.

4. In water **$CaSO_4$** dissolves but sparingly (requiring 500 parts of water), more readily in **HCl** and in **HNO_3,** even dilute, also in a boiling solution of **ammonium sulphate, $(NH_4)_2.SO_4$.**

5. From the aqueous solution **ammonium oxalate** precipitates white **CaC_2O_4.**

6. **Alcohol, C_2H_6O,** renders the gypsum insoluble in water and hence, if added in sufficient quantity, precipitates **$CaSO_4$**.

XIV. CALCIUM PHOSPHATE, $Ca_3(PO_4)_2$.

1. Insoluble in H_2O, easily dissolved by **HCl** or HNO_3. From this acid solution:

2. $NH_4.OH$ reprecipitates calcium phosphate.

3. To the solution in **HCl** add dilute H_2SO_4 and **alcohol.** A white precipitate of $CaSO_4$ results. This is separated by filtration, washed by a little alcohol and dissolved in **HCl** to show the calcium reactions as in **X** and **XIII.**

REACTIONS OF PHOSPHORIC ACID.

4. The phosphoric acid is contained in the filtrate. After boiling this, to expel alcohol, it is examined for phosphoric acid, according to **VII.**

5. The flame is colored green by calcium phosphate; after moistening with **HCl** it shows the orange calcium color. (Easily identified by the spectroscope.)

XV. CALCIUM FLUORIDE. CaF_2.

Fluor Spar.

1. On platinum foil it melts when highly heated.

2. Insoluble in water, soluble in **HCl** and in HNO_3, when it has been finely powdered.

3. Concentrated H_2SO_4 decomposes it, forming **hydro-fluoric acid, HF,** which escapes in gas form, and $CaSO_4$. In this residue the **Ca** reactions are easily shown.

4. **Hydro-fluoric acid, HF,** may be recognized by its pungent odor and by its action on glass or other **silicates.** A small piece of window glass is thinly coated with wax and some portion of it laid bare again, by removing some of the wax with a pin (writing a name or drawing some simple design). In a leaden (or platinum) capsule the CaF_2 is then mixed with H_2SO_4 and the glass placed over the capsule with the engraved side downward. The fumes of the **HF** gas, coming in contact with the bared surface of the glass, corrode it, while the parts protected by wax remain smooth. After removal of the wax, the design shows itself etched upon the glass.

The silicic acid of the glass is converted into **silicon tetrafluoride** gas, SiF_4, and thus removed.

5. If CaF_2 is first mixed with fine sand then placed in a test-

tube and concentrated H_2SO_4 added and gentle heat applied, **silicon tetrafluoride, SiF_4,** escapes which in contact with water forms **silicic acid, H_4SiO_4,** and **hydro-fluo-silicic acid, H_2SiF_6;** hence a glass rod moistened with water and held into the escaping gas, becomes coated with a white film of silicic acid.

$$2CaF_2 + SiO_2 + 2H_2SO_4 = SiF_4 + 2CaSO_4 + 2H_2O.$$

$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6.$$

6. A moistened slip of brazilwood testpaper becomes yellow by the fumes of **HF.**

XVI. ALUMINIUM AMMONIUM SULPHATE.

$Al_2(SO_4)_3.(NH_4)_2SO_4 + 24H_2O.$

Ammonia Alum

1. When heated in a glass tube water is given off, leaving a residue of burnt alum.

2. When mixed with dry sodium carbonate and heated on charcoal in the reduction flame of the blowpipe, it forms **hepar.** For this and other reactions of sulphuric acid see, III. 3. 4. 5.

3. Gives the ammonium reactions. (See V. 2. etc.)

ALUMINUM REACTIONS.

4. Alum is soluble in about 10 parts of cold water: from this solution $NH_4.OH$ precipitates white **aluminium hydrate, $Al_2(OH)_6$,** insoluble in excess of $NH_4.OH$.

5. **NaOH** or **KOH** precipitate $Al_2(OH)_6$, soluble in excess of the precipitant, from which solution it is re-precipitated by NH_4Cl, but not by mere boiling.

6. Na_2CO_3 precipitates $Al_2(OH)_6$, while CO_2 escapes.

$$3Na_2CO_3 + (NH_4)_2SO_4.Al_2(SO_4)_3 + 3H_2O = Al_2(OH)_6 + 3CO_2 + 3Na_2SO_4 + (NH_4)_2SO_4.$$

7. **Ammonium sulphide,** $(NH_4)_2S$ produces a white precipitate of $Al_2(OH)_6$, while H_2S escapes.

$$3(NH_4)_2S + (NH_4)_2SO_4.Al_2(SO_4)_3 + 6H_2O = Al_2(OH)_6 + 3H_2S + 4(NH_4)_2SO_4.$$

8. Heated on charcoal after moistening with **cobaltous nitrate, $Co(NO_3)_2$,** an opaque blue mass results.

XVII. POTASSIUM DICHROMATE, $K_2Cr_2O_7$.

1. When heated in glasstube it melts into a dark red liquid

2. A small crystal heated on charcoal deflagrates slightly, leaving a green residue of **chromic oxide, Cr_2O_3,** and **K_2CO_3**. This residue may be dissolved in water, filtered and the **K** reactions shown in the solution.

CHROMIUM REACTIONS.

3. When a small quantity is introduced into a bead of **borax** or **microcosmic salt** attached to the loop of platinum wire, the bead is colored **green** in the oxidation as well as in the reduction flame.

4. The aqueous solution of **$K_2Cr_2O_7$** shows the presence of **chromic acid** by the following reactions:

H_2S added to the acidulated yellow solution reduces the **chromic acid** to a **green chromic oxide** salt, which remains in solution while **S** precipitates. Warming hastens the reaction.

5. **$(NH_4)_2S$** produces a **brown** precipitate of **$Cr_2(CrO_4)_3$** accompanied by **S.** In the solution yellow **K_2CrO_4** remains. **$5K_2Cr_2O_7 + 3(NH_4)_2S + 3H_2O = Cr_2(CrO_4)_3 + S_3 + 5K_2CrO_4 + 6(NH_4.OH)$**. If the solution be boiled after sufficient **$(NH_4)_2S$** has been added, **green chromic hydrate, $Cr_2(OH)_6$,** and **sulphur** are precipitated. **$K_2Cr_2O_7 + 3(NH_4)_2S + 7H_2O = Cr_2(OH)_6 + 3S + 2KOH + 6(NH_4.OH)$.**

6. **$Pb(C_2H_3O_2)_2$** precipitates **yellow lead chromate, $PbCrO_4$,** insoluble in dilute **HNO_3**, soluble in **NaOH**.

7. **$Hg_2(NO_3)_2$: brickred** precipitate of **mercurous chromate, Hg_2CrO_4.**

8. **$AgNO_3$: dark red** precipitate of **silver chromate, Ag_2CrO_4.**

9. **Sulphurous acid, H_2SO_3** reduces **potassium dichromate** to **green chromic salt.** **$3K_2Cr_2O_7 + 12H_2SO_3 = 2K_2Cr_2(SO_4)_4 + Cr_2(SO_3)_3 + K_2SO_4 + 12H_2O$.** Addition of **$H_2SO_4$** accelerates the reduction.

10. When potassium dichromate is boiled with concentrated **HCl**, free chlorine escapes and a green solution of **Cr_2Cl_6** results. If **alcohol** be added in small quantity, the reduction is accomplished more readily by the formation of **aldehyde** and **Cr_2Cl_6**.

$$K_2Cr_2O_7 + 14HCl = Cr_2Cl_6 + 6Cl + 2KCl + 7H_2O.$$

$K_2Cr_2O_7 + 8HCl + 3C_2H_6O = Cr_2Cl_6 + 2KCl + 3C_2H_4O$ (aldehyde) $+ 7H_2O$.

In the green solution obtained by 9 or 10, or in an aqueous solution of chromic alum, the reactions of **chromic oxide** are obtained as follows:

11. **$NaOH$** precipitates **bluish green chromic hydrate, $Cr_2(OH)_6$**, soluble in excess of **$NaOH$**. By boiling this solution, the precipitate falls again.

12. **NH_4OH** precipitates **grayish blue $Cr_2(OH)_6$** slightly soluble in excess of **NH_4OH** with reddish color.

13. **$(NH_4)_2S$:** green precipitate of **$Cr_2(OH)_6$**.

14. **Na_2CO_3** precipitates green **basic chromic carbonate.**

15. When either of the precipitates are dried and melted with **potassium nitrate** on the platinum foil, the mass assumes a yellow color from the formation of **potassium chromate.**

XVIII. IRON, Fe.

1. A thin iron wire burns before the blowpipe to **ferroso-ferric oxide, Fe_3O_4**

2. In **HCl** iron dissolves, rapidly on heating, **hydrogen** is given off and **carbon** left as residue. **$Fe+2HCl=FeCl_2+H_2$.** **Ferrous chloride $FeCl_2$** is in the solution. As this is not readily purified, it is better to make the

a. REACTIONS OF FERROUS SALTS

with a fresh solution of **ferrous sulphate, $FeSO_4+7H_2O$**, in water. In this pale green solution:

3. **$NaOH$** or **$NH_4.OH$** produces a greenish white precipitate of **ferrous hydrate, $Fe''(OH)_2$**; this rapidly absorbs oxygen from the air and becomes first green, then brown, forming **ferric hydrate, $Fe_2(OH)_6$.** **$2Fe(OH)_2+O+H_2O=Fe_2(OH)_6$.**

4. **Na_2CO_3** precipitates white **ferrous carbonate, $FeCO_3$**, which becomes brown in contact with air.

5. **H_2S** produces no precipitate in a solution rendered acid by a little **HCl**.

6. **$(NH_4)_2S$** produces a black precipitate of **ferrous sulphide, FeS**, which is decomposed by **HCl** forming **$FeCl_2$** and **H_2S.**

7. **Ferro-cyanide of potassium, $K_4Fe''(CN)_6$**, (yellow prussiate of potash) produces in **ferrous salts** a **bluish-white** precipitate of **potassium ferrous ferrocyanide, $K_2Fe''_2(CN)_6$**, which will become **dark blue** rapidly, when in contact with air.

8. **Ferri-cyanide of potassium, $K_6Fe'''_2(CN)_{12}$**, (red prussiate

of potash) produces at once a dark blue precipitate of **Turnbull's blue**, $Fe''_3(CN)_6.Fe'''_2(CN)_6$.

9. **Sulphocyanide of potassium**, $KCNS$, does not alter **ferrous** salts.

10. To the **pale-green** solution of **ferrous sulphate**, $Fe''SO_4$, add H_2SO_4 and nitric acid. At first a brown-black color appears ($2FeSO_4.NO$, see IV. 8.), which is converted into yellow by boiling. The solution then contains **ferric sulphate**, $Fe'''_2(SO_4)_3$, while NO escapes. $6FeSO_4+3H_2SO_4+2HNO_3=3Fe_2(SO_4)_3+2NO+4H_2O$.

b. REACTIONS OF FERRIC SALTS.

11. **Ferric chloride**, Fe'''_2Cl_6, is very suitable for these reactions. From its solution, $NaOH$ or $NH_4.OH$ precipitates brown-red **ferric hydrate**, $Fe'''_2(OH)_6$.

12. Na_2CO_3 precipitates from Fe'''_2Cl_6 also **ferric hydrate**, $Fe_2(OH)_6$, while CO_2 escapes.

13. H_2S produces in an acid solution of **ferric chloride** a white precipitate of S, while the **ferric** salt is reduced to **ferrous chloride**, $Fe''Cl_2$.

14. $(NH_4)_2S$ precipitates black **ferrous sulphide**, FeS, and S.

15. **Ferro-cyanide of potassium**, $K_4Fe(CN)_6$, (yellow prussiate) precipitates dark blue, **prussian blue**, $Fe''_3(CN)_6.Fe'''_4(CN)_{12}$. **Caustic alkalies**, $NaOH$, or KOH, destroy the color and form a yellow solution.

16. **Ferri-cyanide of potassium**, $K_6Fe_2(CN)_{12}$, (**red prussiate**), when recently dissolved, gives a deep brown color to solutions of **ferric** salts, but no precipitate.

17. **Potassium sulphocyanide**, $KCNS$, produces even in very dilute solutions of ferric salts a deep red color of **ferric sulphocyanide**, $Fe_2(CNS)_6$.

18. To a small quantity of **ferric chloride** in **neutral** solution add an excess of **sodium acetate**, $NaC_2H_3O_2$. The solution becomes deep red from the formation of **ferric acetate**. On boiling all the iron precipitates as pale brown **basic ferric acetate**, while the solution becomes colorless.

19. **Barium carbonate**, $BaCO_3$, suspended in water, precipitates from **ferric** salts $Fe_2(OH)_6$, while CO_2 escapes.

20. A small portion of any dry iron salt, or any of the foregoing precipitates of ferric hydrate, is heated before the blow-

pipe with **microcosmic salt.** In the **reduction flame** the bead will look **green,** while hot, in the **oxidation** flame **red.** On cooling the color fades, and when very small quantities of **Fe** are present, the bead becomes colorless.

XIX. MANGANOUS SULPHATE, $MnSO_4+7H_2O$.

1. In the glass tube, on heating, water is given off.

2. It colors the **microcosmic** bead violet red in the oxidation flame, when cool, the color is amethystine. In the reduction flame the bead loses its color.

3. H_2S does not precipitate the acidulated, pink colored. solution.

4. $(NH_4)_2S$ produces a **flesh colored** precipitate of hydrated **manganous sulphide,** $MnS.H_2O$, which darkens in contact with air, and by boiling loses water and becomes green, if NH_4OH or $(NH_4)_2S$ be present in excess, and NH_4Cl absent. HCl dissolves the precipitate.

5. $NaOH$ precipitates **white manganous hydrate,** $Mn(OH)_2$, which rapidly absorbs **O** from the air and turns brown. (NH_4OH forms this precipitate only if NH_4Cl is absent.)

6. Na_2CO_3 precipitates white **manganous carbonate,** $MnCO_3$.

7. When a trace of any manganese compound such as **manganese dioxide,** MnO_2, (black oxide of manganese) is melted on the platinum foil with Na_2CO_3 and some KNO_3, a green-blue mass results, containing **sodium manganate,** Na_2MnO_4.

Sulphuric acid reactions as before.)

XX. POTASSIUM PERMANGANATE, $KMnO_4$.

1. Heated in a glass tube it decrepitates.

2. It dissolves in water with a deep red purple color.

3. H_2S discharges the color of the solution acidulated with sulphuric acid leaving white sulphur suspended in the liquid.

4. $(NH_4)_2S$ precipitates **manganous sulphide,** MnS, together with **S.**

5. When sufficient **oxalic acid,** $H_2C_2O_4$, is added to a dilute permanganate solution, previously acidulated with sulphuric acid, the color is entirely discharged. $2KMnO_4+5H_2C_2O_4+3H_2SO_4=K_2SO_4+2MnSO_4+10CO_2+8H_2O$.

6. Freshly prepared solution of **$FeSO_4$** decolorizes a dilute solution of permanganate, acidulated with **H_2SO_4.** **$10Fe''SO_4+2KMnO_4+8H_2SO_4=5Fe'''_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O$.**

7. **HCl** decomposes **$KMnO_4$** with liberation of **chlorine.**

8. When a small crystal of **$KMnO_4$** is thrown into a small quantity of **concentrated** sulphuric acid, heated in a test tube, a violent reaction ensues, red vapors of **permanganic acid, $HMnO_4$,** arise and condense in the upper part of the tube, while small fragments of the crystal, heated to a red heat, are projected from the liquid. For other **Mn** reactions compare XIX, and for **K** reactions, see IV. The absorption spectrum of **$K\,Mn\,O_4$** shows 5 characteristic bands in yellow and green, (see table.)

XXII. ZINC. Zn.

1. When metallic **zinc** is heated before the blowpipe, on charcoal, it burns with a brilliant bluish-green flame, forming white fumes of **zinc oxide, ZnO.** A portion of this coats the charcoal and is of **yellow** color while hot, but **white** when cool. It is not volatile.

2. Zinc dissolves readily in dilute sulphuric acid or in hydrochloric acid evolving hydrogen gas.

$Zn+2HCl=ZnCl_2+2H$.

To obtain a suitable solution for showing the reactions of zinc, boil a surplus of zinc with hydrochloric acid, dilute with water and filter. Or else dissolve **zinc sulphate, $ZnSO_4+7H_2O$,** in water.

3. **NaOH** precipitates white **zinc hydrate, $Zn(OH)_2$,** which redissolves in excess of the precipitant. **$Zn(OH)_2+2NaOH=ZnNa_2O_2+2H_2O$.**

4. **Ammonium hydrate** produces a similar precipitate, if no ammonium salts are present, for these as well as an excess of ammonium hydrate dissolve the **$Zn(OH)_2$.**

5. **Na_2CO_3**: white précipitate of **basic zinc carbonate, $2ZnCO_3+3[Zn(OH)_2]+4H_2O$,** while **$CO_2$** escapes. Insoluble in excess.

6. **Ammonium carbonate** precipitates white **basic zinc carbonate,** soluble in excess. On boiling the dilute solution **$Zn(OH)_2$** is precipitated, unless ammonium salts or other solvents prevent it.

7. From **neutral** solutions of zinc salts H_2S precipitates white **hydrated zinc sulphide, $ZnS.H_2O$**, but not completely. The presence of free **HCl** or other acids prevents this; from **acetate of zinc**, even when **free acetic acid** is present, the whole of the zinc is precipitated.

8. $(NH_4)_2S$ precipitates **ZnS**, insoluble in acetic acid $H.C_2H_3O_2$ soluble in **HCl**.

9. If some zinc salt is moistened with **cobaltous nitrate, $Co(NO_3)_2$**, and heated before the blowpipe, on charcoal, a bright **green** mass is formed.

XXII. NICKELOUS SULPHATE. $NiSO_4 + 7H_2O$.

The green salt dissolves readily in water and yields the following reactions:

1. **NaOH** precipitates green **nickelous hydrate, $Ni(OH)_2$**, insoluble in excess of reagent, soluble in ammonium salts.

2. NH_4OH also precipitates $Ni(OH)_2$, soluble in excess of NH_4OH with blue color. The presence of sugar, or citric, or tartaric acid interferes with the above precipitates.

3. Na_2CO_3: green precipitate of basic carbonate,

$$2NiCO_3.3Ni(OH)_2.$$

4. $(NH_4)_2CO_3$: green precipitate, soluble in excess of reagent.

5. H_2S, no precipitate in acid or neutral solutions (excepting partial precipitation of acetate).

6. $(NH_4)_2S$, black precipitate of **NiS**, slightly soluble in excess of precipitant, insoluble in dilute **HCl**.

7. **Potassium cyanide, KCN**, precipitates pale green $Ni(CN)_2$ soluble in excess, **HCl** reprecipitates $Ni(CN)_2$ even after boiling.

8. The microcosmic bead is, by addition of a nickel compound, colored red in the oxidation flame, while hot, and becomes paler on cooling. In the reduction flame the color appears yellow, and, if tinfoil is added, gray.

XXIII. COBALTOUS NITRATE. $Co(NO_3)_2$ $6H_2O$.

The rose-red salt dissolves readily in water.

1. **NaOH** precipitates **blue** basic salt, which becomes pale red $Co(OH)_2$ by boiling, mixed with more or less brownish-green Co_3O_4 by the action of air during protracted boiling. Sugar and organic acids prevent precipitates.

2. **NH_4OH** yields same **blue** precipitate as caustic soda, soluble in excess of precipitant, with red color, from the formation of **$Co(NO_3)_2.(NH_3)_6$.**

3. **H_2S,** no precipitate.

4. **$(NH_4)_2S$,** black precipitate of **cobaltous sulphide, CoS,** insoluble in dilute **HCl.**

5. **Na_2CO_3, peach bloom** colored basic **cobaltous carbonate,** soluble in ammonium carbonate.

6. **Potassium nitrite, KNO_2,** added to cobalt solution acidulated with acetic acid, produces slowly a **yellow** precipitate of **potassium cobaltic nitrite, $Co_2(NO_2)_6.6KNO_2$. $2Co(NO_3)_2+12KNO_2+2H.C_2H_3O_2 = Co_2(NO_2)_6.6KNO_2+4KNO_3+2KC_2H_3O_2$.** This reaction serves to recognize **Co, K,** and **HNO_2**; compare IV., 7.

7. **Potassium cyanide, KCN,** precipitates red-brown **cobaltous cyanide, $Co(CN)_2$,** soluble in excess. **HCl** reprecipitates the cobaltous cyanide, unless it has been previously boiled with excess of **KCN** and a few drops of **HCl.** In that case **potassium cobalti-cyanide, $K_6Co_2(CN)_{12}$,** is formed, in which the acid will form no precipitate.

8. To a dilute solution of **cobaltous nitrate** add first **tartaric** or **citric acid,** then an excess of **ammonia water** and lastly a few drops of **potassium ferri-cyanide. A deep red** color appears visible even in great dilution.

9. Borax and microcosmic beads are colored blue by heating with cobalt in any part of the flame.

XXIV. LEAD. Pb.

1. Heated on charcoal before the blowpipe it melts. In the outer oxidation flame it is converted into lead monoxide, which volatilizes and leaves a yellow coating on the charcoal.

2. If a small quantity of **litharge,** (lead monoxide) is heated on charcoal in the inner, reducing flame of the blowpipe, lead is readily reduced and forms a metallic globule.

3. Metallic lead is insoluble in **HCl** and in **H_2SO_4.** In **HNO_3** it dissolves with evolution of **NO. $3Pb+8HNO_3=3Pb(NO_3)_2+2NO+4H_2O$.**

4. **Red lead, Pb_3O_4,** is insoluble in water. When **HCl** is added **$PbCl_2$** is formed, (soluble in much boiling water, see I. 5.)

while **chlorine** is set free.

5. To red lead add HNO_3 and H_2O: $Pb(NO_3)_2$ is formed, soluble in water and **brownish-purple lead dioxide, PbO_2,** is left as insoluble residue.

The lead reactions may be studied in the following:

XXV. LEAD ACETATE. $Pb(C_2H_3O_2)_2$.

Sugar of lead.

a. REACTIONS OF LEAD.

1. When heated in glasstube, first water is given off, then acetic acid; the black residue contains C and metallic lead.

2. Heated before the blowpipe on charcoal, with dry Na_2CO_3, a ductile globule of metallic lead is obtained and a yellow encrustation of **PbO.**

3. It dissolves readily in water. Metallic zinc precipitates **Pb** in crystals, (lead tree).

4. H_2S and $(NH_4)_2S$ precipitates black **lead sulphide, PbS,** insoluble in acids; when boiled with concentrated nitric acid it is converted into **white $PbSO_4$.**

5. H_2SO_4, or soluble sulphates, give a white precipitate of $PbSO_4$, insoluble in acids (excepting **concentrated** H_2SO_4, in which it dissolves to some extent, but is precipitated by dilution with water). It also dissolves in an ammoniacal solution of tartaric acid. $(NH_4)_2S$ converts $PbSO_4$ into **PbS.**

6. **NaOH** precipitates white **plumbic hydrate, $Pb(OH)_2$,** soluble in large excess of **NaOH.**

7. NH_4OH: white precipitate of basic salt, insoluble in excess.

8. Na_2CO_3: white precipitate of **lead carbonate, $PbCO_3$.**

9. **HCl**: white $PbCl_2$, soluble in 33 parts of boiling, and in 135 parts of cold water.

10. $K_2Cr_2O_7$: yellow precipitate of **lead chromate, $PbCrO_4$,** insoluble in dilute nitric acid, soluble in **NaOH.** (see XVII. 6.)

b. REACTIONS OF ACETIC ACID.

11. Heat $Pb(C_2H_3O_2)_2$ with H_2SO_4 in a testtube, **acetic acid,** $HC_2H_3O_2$ is liberated, recognized by odor and by reddening blue litmus paper held in the fumes.

12. To the **lead acetate** add **alcohol** and **sulphuric acid** in

about equal volumes and heat. **Acetic ether** (ethyl acetate), **$C_2H_5.C_2H_3O_2$**, is formed, easily recognized by its odor, (compare also XVIII. 18. for test of acetic acid by ferric chloride).

XXVI. BISMUTH. Bi.

1. Heated in glasstube it melts, without volatilizing. The metal has a pinkish lustre and a crystalline texture.

2. Before the blowpipe, on charcoal it melts to a brittle globule, while **yellow oxide, Bi_2O_3**, coats the surrounding charcoal.

3. When a small portion of **Bi** or its compounds is mixed with **sulphur** and **potassium iodide**, and heated before the blowpipe on charcoal, a **bright scarlet red** encrustation will form.

4. In concentrated **HNO_3** bismuth will dissolve with copious evolution of **NO**, while **nitrate, $Bi(NO_3)_3$** forms. **$Bi + 4HNO_3 = Bi(NO_3)_3 + NO + 2H_2O$.**

5. Into a testtube, half filled with **H_2O**, drop some of the solution of **$Bi(NO_3)_3$**. A white precipitate of **bismuth subnitrate, $BiNO_3.(OH)_2$**, falls. **$Bi(NO_3)_3 + 2H_2O = BiNO_3.(OH)_2 + 2HNO_3$.** If the solution contains much **free HNO_3**, the precipitate forms on addition of **NaCl** or **HCl**. In that case it contains **bismuth oxy-chloride, BiOCl. $Bi(NO_3)_3 + 3NaCl + H_2O = BiOCl + 3NaNO_3 + 2HCl$.**

6. **H_2S** and **$(NH_4)_2S$** precipitate brownish-black **Bi_2S_3** insoluble in dilute acids or in ammonium sulphide.

7. **NaOH** and **$NH_4.OH$** precipitate white **bismuth hydrate, $Bi(OH)_3$** insoluble in excess.

8. **Potassium dichromate** precipitates yellow **$Bi_2O(CrO_4)_2$**, insoluble in **NaOH**, soluble in nitric acid. **$2Bi(NO_3)_3 + K_2Cr_2O_7 + 2H_2O = Bi_2O(CrO_4)_2 + 2KNO_3 + 4HNO_3$.**

XXVII. COPPER SULPHATE. $CuSO_4 + 5H_2O$.

Blue vitriol.

1. When a bright piece of iron or zinc is dipped into the solution, red **metallic copper** precipitates upon them, while iron or zinc sulphate is formed in the solution.

2. **NaOH** precipitates from the solution **pale-blue cupric hydrate, $Cu(OH)_2$**, insoluble in excess; on heating it loses **H_2O** and becomes **black cupric oxide, CuO.** If to a dilute solution

of **cupric sulphate, $CuSO_4$**, **glucose** is added and then **NaOH**, the pale blue precipitate, first formed, is redissolved by an excess of **NaOH**; on heating yellow **cuprous hydrate, $Cu_2(OH)_2$**, separates, which, by boiling, loses **H_2O** and becomes **red cuprous oxide, Cu_2O**.

3. **NH_4OH** produces a greenish-blue precipitate of a basic salt. This dissolves in an excess of **NH_4OH** with deep azure-blue color, recognizable even in very great dilution. The compound formed is **cupro-diammonium sulphate. $(N_2H_6Cu).SO_4$**.

4. **H_2S** precipitates black **cupric sulphide, CuS**, insoluble in dilute acids and in caustic alkalies, soluble in boiling nitric acid.

5. **$(NH_4)_2S$** produces the same precipitate of **CuS**, slightly soluble in excess, especially if **yellow ammonium sulphide** is used.

6. The precipitated **CuS** is filtered off and tested before the blowpipe on charcoal. A portion is mixed with dry **Na_2CO_3** and heated, the melted mass is removed to an agate mortar and triturated with water. After washing off the charcoal particles, shining, red, crystalline scales of copper remain.

7. Another portion of **CuS** is attached to the bead of microcosmic salt on the platinum wire. In the **oxidation** flame a **green** bead is obtained, which becomes **blue** on cooling. On adding a little **tinfoil, Sn**, to this bead and heating it in the **reduction** flame, it becomes **opaque** and **red**, from the reduction of the **cupric** to the **cuprous** oxide by means of **Sn**.

8. **Potassium ferro-cyanide, $K_4Fe(CN)_6$**, produces in neutral or **acidulated** solution of copper salts a red-brown precipitate of **cupric ferro-cyanide, $Cu_2Fe(CN)_6$**, which is insoluble in acids, but is readily decomposed by alkalies.

9. To the copper solution add first **sulphurous acid, H_2SO_3**, then **KCNS** (or **$NH_4.CNS$**): a white precipitate of **cuprous sulpho-cyanide, $Cu_2(CNS)_2$**, is formed.

10. **Potassium cyanide, KCN**, forms a greenish precipitate, soluble in excess of **KCN**. From this solution **H_2S** does **not** precipitate **CuS**.

XXVIII. CADMIUM SULPHATE. $CdSO_4 + 4H_2O$.

1. Heated on charcoal, before the blowpipe, with dry **Na_2CO_3**, it is reduced and the metal at once converted into **cadmium oxide, CdO**, which gives a brown coating to the charcoal.

2. It is soluble in water; from the solution zinc reduces metallic **Cd**.

3. **H_2S** or **$(NH_4)_2.S$** precipitates from acid, neutral or alkaline solutions **yellow sulphide CdS**, insoluble in **$NH_4.OH$,$(NH_4)_2CO_3$, and in $(NH_4)_2S$** and in dilute acids.

4. **NaOH** precipitates white **cadmium hydrate, $Cd(OH)_2$**, insoluble in excess.

5. **$NH_4.OH$** precipitates white **$Cd(OH)_2$** readily soluble in excess.

6. **Na_2CO_3** precipitates white **cadmium carbonate, $CdCO_3$.**

7. **KCN:** white **cadmium cyanide, $Cd(CN)_2$**, soluble in excess, forming **potassium-cadmium cyanide, $Cd(CN)_2.2KCN$.** From this solution **H_2S** precipitates **yellow CdS.** (distinction from **Cu.**)

XXIX. MERCURY. Hg.

Quicksilver.

a. REACTIONS OF MERCUROUS COMPOUNDS.

1. A solution of **mercurous nitrate, $Hg_2(NO_3)_2$**, is easily prepared by dissolving metallic mercury, in excess, in cold dilute nitric acid, expelling the nitric oxide fumes by gentle heating and pouring the solution off from the residue of undissolved mercury.

2. A drop of this solution placed on bright copper foil produces a silvery spot of metallic **Hg.**

3. **H_2SO_3** precipitates gray metallic **Hg.**

4. **H_2S** or **$(NH_4)_2S$** precipitates a black mixture of **HgS** with **Hg.**

5. **NaOH:** black **mercurous oxide, Hg_2O.**

6. **NH_4OH** precipitates black **mercuros-ammonium nitrate, $NHg_2H_2NO_3$.**

7. **HCl:** white **Hg_2Cl_2, Calomel.**

8. **Potassium iodide, KI:** greenish-yellow **mercurous iodide Hg_2I_2.** If an excess of **KI** be added, soluble **potassium-mercuric iodide, $2KI.HgI_2$**, is formed and metallic **Hg** remains as a gray powder.

9. **$K_2Cr_2O_7$:** orange **mercurous chromate, Hg_2CrO_4.**

b. REACTIONS OF MERCURIC COMPOUNDS.

To the solution of mercurous nitrate some **HCl** and **HNO_3** are added and heat applied until the white precipitate of calomel is re-dissolved and the acids expelled. Or else **corrosive sublimate, $HgCl_2$** is dissolved in water.

10. From this solution of **mercuric chloride, $HgCl_2$,** copper precipitates metallic **Hg.**

11. A dilute solution of **stannous chloride, $SnCl_2$,** added carefully drop by drop produces at first a white precipitate of **Hg_2Cl_2,** further addition of the reagent reduces this to gray metallic **Hg.**

12. **NaOH** added in small quantity produces a brown precipitate of basic salt, which, on addition of more **NaOH** passes into **yellow mercuric oxide, HgO.**

13. **NH_4OH** precipitates white **chloride of mercur-ammonium, NH_2HgCl.**

14. **Na_2CO_3** produces a reddish brown precipitate of **basic carbonate, $HgCO_3.3HgO$.**

15. **H_2S,** or **$(NH_4)_2S$,** added sparingly, produces at first a white precipitate of **$2HgS.HgCl_2$;** on farther addition of either reagent this is converted into black **HgS.**

16. **KI** precipitates **HgI_2,** which is at first yellow, but soon turns scarlet. It is soluble in excess of **KI,** or of **$HgCl_2$.**

17. **HCl:** no precipitate.

18. $K_2Cr_2O_7$: red precipitate of **mercuric chromate, $HgCrO_4$.**

19. When any of the above precipitates are heated in the glasstube with dry **$NaCO_3$,** a sublimate of metallic **Hg** will form in the upper part of the tube, in which minute globules may be recognized by the magnifying lens: they will coalesce by rubbing with a glass-rod.

XXX. SILVER NITRATE. $AgNO_3$.

Lunar Caustic.

1. The white crystals dissolve in **H_2O;** paper or fingers stained with the solution soon turn black, from reduction of **Ag.**

2. Metallic copper, zinc or iron precipitate metallic silver, while their nitrates are found in the solution.

3. **H_2S** and **$(NH_4)_2S$** precipitate black **silver sulphide, Ag_2S,** insoluble in dilute acids, in alkalies, alkaline sulphides, and in potassium cyanide: soluble in boiling nitric acid.

4. **$NaOH$:** dark brown precipitate of **argentic oxide, Ag_2O,** insoluble in excess.

5. **NH_4OH:** brown precipitate, **Ag_2O,** readily soluble in excess of **NH_4OH.** If ammonium salts or free acid are present in solution, **NH_4OH** fails to give a precipitate.

6. **Na_2CO_3:** yellow precipitate of **silver carbonate, Ag_2CO_3.**

7. **Na_2HPO_4:** yellow precipitate of **silver phosphate, Ag_3PO_4,** soluble in **NH_4OH** and in **HNO_3.**

8. **HCl:** white curdy **$AgCl$.** (see 1, 3.)

9. **$K_2Cr_2O_7$:** brownish-red precipitate of **Ag_2CrO_4,** decomposed by addition of **HCl** into white **$AgCl$.**

10. No precipitate is produced by **dilute sulphuric acid.** (Distinction from lead compounds.)

XXXI. TIN. Sn.

1. Heated on charcoal, before the blowpipe, it melts and in the oxidation flame is converted into white **stannic oxide, SnO_2.**

2. Dissolves easily by boiling in concentrated **HCl,** while **H** escapes. The solution contains **stannous chloride, $SnCl_2$.**

a. REACTIONS OF STANNOUS COMPOUNDS.

3. From a solution of **stannous chloride, $SnCl_2$,** zinc precipitates metallic **Sn.**

4. **$NaOH$:** white **stannous hydrate, $Sn(OH)_2$,** soluble in excess of **$NaOH$.**

5. **NH_4OH:** white **$Sn(OH)_2$,** insoluble in excess of **NH_4OH.**

6. **Na_2CO_3:** white **$Sn(OH)_2$,** while **CO_2** escapes.

7. **H_2S** and **$(NH_4)_2S$** precipitate from neutral or acidulated solutions dark brown **stannous sulphide, SnS. Large excess of HCl** prevents the precipitation. The precipitate is nearly insoluble in **colorless $(NH_4)_2S$,** but readily dissolves in **yellow $(NH_4)_2S_2$.*** From this solution **HCl** precipitates yellow **stannic sulphide, SnS_2. $SnS + (NH_4)_2S_2 = SnS_2 + (NH_4)_2S$.**

8. **$HgCl_2$:** converts **$SnCl_2$** into **$SnCl_4$** while, according to the relative quantity, either **Hg_2Cl_2** or metallic **Hg** are precipitated. (See XXIX, 11.)

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* Freshly prepared ammonium sulphide is colorless and consists of $(NH_4)_2S$. When it is digested with powdered sulphur, or kept in vessels partially filled with air, or opened frequently, it becomes yellow from the formation of ammonium disulphide. $2(NH_4)_2S + O + H_2O = (NH_4)_2S_2 + 2NH_4OH$. By farther oxidation polysulphides and finally hyposulphite are formed.

b. REACTIONS OF STANNIC COMPOUNDS.

9. When **Sn** is heated with **HNO_3** a white powder is produced, insoluble in water or in cold acids. This is **meta-stannic acid, $H_{10}Sn_5O_{15}.5H_2O$.** When this is washed and then boiled for some time with **HCl** it is converted into **stannic chloride, $SnCl_4$;** the same result is obtained by dissolving tin in nitro-muriatic acid at once, or by distilling tin with corrosive sublimate.

10. An aqueous solution of **stannic chloride, $SnCl_4$,** shows the following reactions:

NaOH precipitates white **stannic hydrate, $SnO_2.H_2O$,** (stannic acid, **H_2SnO_3**) soluble in excess of **NaOH.**

11. **NH_4OH:** white precipitate of **$SnO_2.H_2O$,** insoluble in excess.

12. Diluting the solution of **$SnCl_4$** strongly with water and boiling produces a white precipitate of **$SnO_2.H_2O$.**

13. **$HgCl_2$:** no precipitate.

14. **H_2S:** yellow precipitate, soluble in **$(NH_4)_2S$.**

15. When either of the precipitates obtained in 9, 10, 11 or 12 is dried, mixed with dry **Na_2CO_3,** and heated in the reduction flame of the blowpipe, on charcoal, metallic globules of tin are produced.

16. A mixture of **stannous** with **stannic chloride** is precipitated by **gold chloride, $AuCl_3$,** with a purple color, seen even in great dilution and called **purple of Cassius.**

XXXII. ANTIMONY. Sb.

1. Metallic antimony has a crystalline texture, a bluish lustre, is hard and brittle and melts in the ignition tube without volatilizing.

2. Before the blowpipe, on charcoal, it melts and forms a white volatile incrustation of **antimonous oxide** (trioxide) **Sb_2O_3.** The hot metallic globule continues to burn after withdrawal from the flame, it emits white fumes and covers itself with white crystalline needles of **Sb_2O_3.**

3. In **HCl** it is insoluble: **HNO_3** converts it into insoluble white **met-antimonic acid, $HSbO_3$,** which, when heated nearly to redness, becomes yellow **antimonic oxide** (pentoxide), **Sb_2O_5. $2HSbO_3=Sb_2O_5+H_2O$.**

4. In **nitro-muriatic** acid metallic antimony dissolves readily. If dilute acid and excess of antimony be used **antimonous chloride, $SbCl_3$,** is formed. If the acid is used concentrated and in excess, **antimonic chloride, $SbCl_5$,** is found in the solution.

5. From the solution of **antimonous chloride, $SbCl_3$,** water precipitates **antimonous oxychloride** (powder of Algaroth) **$SbOCl$,** which is readily soluble in **tartaric acid, $H_2.C_4H_4O_6$,** which, when mixed with water prevents its precipitation.

6. From the solution of **antimonic chloride, $SbCl_5$,** much water precipitates **pyro-antimonic acid, $H_4Sb_2O_7$,** as a white powder.

7. **H_2S** and **$(NH_4)_2S$** precipitate from acidulated solutions of antimonous salts **orange antimonous sulphide, Sb_2O_3,** soluble in excess of **$(NH_4)_2S$** or in **NH_4OH,** or in **K_2S,** but **not** in **$(NH_4)_2CO_3$**. From these solutions the sulphide is again precipitated by dilute **HCl**. (From antimonic salts a similar precipitate of **Sb_2S_5,** mixed with **Sb_2S_3** and with sulphur, is thrown down).

8. From antimonous chloride **$NaOH$** precipitates white **antimonous hydrate, $Sb(OH)_3$,** soluble in excess of precipitant.

9. **NH_4OH** precipitates the same **$Sb(OH)_3$** insoluble in **NH_4OH.**

10. Zinc precipitates metallic **Sb**. If a drop of a solution of antimony be placed upon platinum foil and a piece of zinc held into the solution, a black spot of reduced metallic antimony adheres closely to the platinum, and may be dissolved away by **HNO_3.**

XXXIII. ARSENIC, As, and ARSENIC TRIOXIDE, As_2O_3.

1. Before the blowpipe, on charcoal, **As** gives white fumes of **As_2O_3; As_2O_3** volatilizes unchanged. Both give off a garlicky odor.

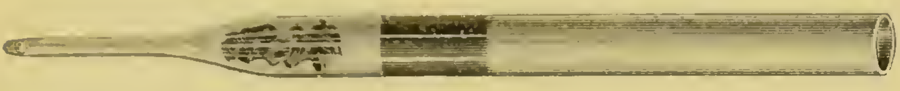
2. When **As** is heated in a glasstube, it sublimes without melting, and deposits on the cooler part of the tube as a black shining ring, **arsenical mirror.** By the presence of air in the tube a small portion is oxidized to **As_2O_3** which deposits itself in minute white crystals.

3. **As_2O_3,** heated in glasstube, sublimes without melting, and without odor, and deposits the same crystals as above. The microscope shows them to be principally regular octohedra.

4. By a small quantity of dilute nitric acid **As** is converted

into As_2O_3, sparingly soluble in water, forming **arsenous acid, H_3AsO_3**; with an excess of hot concentrated HNO_3 **As** is converted into As_2O_5, easily soluble in water, forming **arsenic acid, H_3AsO_4**.

5. Into an **arsenic tube**, (a tube made of hard, Bohemian glass, of 6 to 8 Mm. in diameter and 110 Mm. in length, drawn out into a long tapering point, closed at the end, (fig. 4.)


As_2O_3 Charcoal. Arsenic Mirror. FIG. 4.

a small fragment of As_2O_3 is inserted, so as to be near the closed narrow end. Freshly burnt charcoal, in coarse grains is placed above it, so as to lodge at the widest part of the taper, and occupy about 10 Mm. above the taper. The tube is held at right angles across a flat flame, and is heated at the part containing the charcoal, keeping the point with the As_2O_3 outside the flame until the charcoal becomes red hot. Then the tube is turned into the axis of the broad flame, so as to heat both arsenic and charcoal, still keeping the cylindrical, open end cool and elevated above the point. The As_2O_3 in the point is volatized and ascends through the red-hot charcoal, which deprives it of **O** and converts it into **As**: this forms a mirror in the upper, cooler part of the tube. Instead of charcoal, some dry cyanide of potassium, **KCN**, may be mixed with the As_2O_3, placed at the bottom of a common ignition tube, and heated. A mirror will result.

6. As_2O_3 dissolves very slowly and sparingly in cold, more readily in boiling water (in 15 parts). In dilute **HCl** it dissolves more easily.

7. Put a drop of the aqueous solution of As_2O_3 on a bright piece of copper foil, add a drop of dilute **HCl** and heat gently. A dark steel gray precipitate of **As** will adhere to the copper.

8. To the aqueous solution of As_2O_3 add H_2S. A yellow coloration will result, but no precipitate until some **HCl** is added, when yellow **trisulphide of arsenic, As_2S_3** will separate. This is soluble in $(NH_4)_2S$, in NH_4OH and in $(NH_4)_2CO_3$. Acids precipitate it again from these solutions.

9. **$(NH_4)_2S$:** no precipitate, unless the aqueous solution be rendered acid, (by **HCl**) when **As_2S_3** will fall.

10. **$AgNO_3$:** no precipitate from aqueous solution. When a drop of **NH_4OH** is added yellow **silver arsenite, Ag_3AsO_3,** separates, soluble in **NH_4OH** and in **HNO_3.** When the ammoniacal solution is heated to boiling, metallic silver separates: this serves to distinguish **arsenite, Ag_3AsO_3,** from **arsenate, Ag_3AsO_4** from which no silver is reduced. **$3Ag_3AsO_3 + 6(NH_4OH) = Ag_3AsO_4 + 2[(NH_4)_3AsO_4] + 6Ag + 3H_2O$.**

REACTIONS OF ARSENIC ACID.

11. **As_2O_3** dissolves when boiled in **HNO_3.** The solution contains **ortho-arsenic acid, H_3AsO_4.**

12. When **H_2S** is added in excess to this solution and heat applied yellow **arsenic pentasulphide, As_2S_5,** is precipitated.

13. **$AgNO_3$** does not precipitate the solution until it is neutralized carefully with **NH_4OH;** in that case reddish brown **silver arsenate, Ag_3AsO_4,** precipitates, easily soluble in **NH_4OH** and in **HNO_3.**

14. On addition of excess of **NH_4OH, NH_4Cl** and **$MgSO_4$** a white precipitate of **magnesium ammonium arsenate, $Mg(NH_4)AsO_4$** is formed. This reaction closely resembles that of phosphoric acid, compare VII. 5.

The recognition of small quantities of **arsenic** by **Marsh's method** and its separation from **antimony** will be described farther on, in the systematic course of analysis.

XXXIV. POTASSIUM CHLORATE. $KClO_3$.

1. When heated in ignition tube, **$KClO_3$,** melts and, at higher heat, gives off its **O,** which may be recognized by rekindling a glowing splinter of wood, held into the tube above the melted salt. The residue consists of **potassium chloride, KCl,** which is readily soluble in water and gives the reactions for chlorine by silver nitrate, mercurous nitrate and lead acetate as described in I., 3. 4. 5.

2. On heating a small crystal of **$KClO_3$** before the blowpipe, on charcoal, it deflagrates violently.

3. Into a testtube containing a few drops of concentrated **H_2SO_4** place a very small crystal of **$KClO_3$.** Yellow **chlorine tetroxide** gas, **Cl_2O_4,** is evolved, which detonates with violence

on warming. The crystal becomes brownish yellow, and contains **potassium perchlorate, $KClO_4$.**

$3KClO_3 + 2H_2SO_4 = Cl_2O_4 + KClO_4 + 2KHSO_4 + H_2O$.

Great caution must be exercised in the two last experiments that no damage ensue from the deflagration and the detonation by the flying about of the heated particles of salt or of acid. Hence only very small quantities should be employed and the tube so held that particles ejected from it do not injure anything.

4. Heat **$KClO_3$** with **HCl:** a yellowish green gas results, containing **Cl** and **Cl_2O_4.**

5. **$KClO_3$** requires 16.5 parts of cold, and only 2 parts of boiling water to dissolve it

6. In the aqueous solution **$AgNO_3$** and **$Hg_2(NO_3)_2$** occasion no precipitates unless **KCl** is present as impurity.

7. To the solution of **$KClO_3$** add a few drops of **indigo solution,** a little **H_2SO_4** and then, drop by drop, **sulphurous acid, H_2SO_3.** In consequence of the formation of lower oxides of chlorine, the blue color is discharged.

8. To a solution of **aniline sulphate,** in **H_2SO_4,** add a trace of **$KClO_3$,** the liquid at once becomes **blue.** (Hypochlorites give the same reaction, but nitrates color the aniline sulphate red.)

XXXV. SODIUM SILICATE. Na_4SiO_4.

Soluble glass.

1. From its aqueous solution **HCl** or **HNO_3,** when gradually added, precipitate gelatinous **soluble silicic acid, H_4SiO_4,** which dissolves on addition of much water.

2. **NH_4Cl** or **$(NH_4)_2CO_3$** precipitate even from dilute solutions of sodium silicate **H_4SiO_4,** while **NH_3** escapes.

3. When the solution of **Na_4SiO_4** is acidulated with **HCl,** evaporated to dryness, the residue boiled with water and a few drops of **HCl,** the soluble **silicic acid** is converted into insoluble **silicon dioxide, SiO_2.**

4. Separate **SiO_2** by filtration and add some of it to a bead of microcosmic salt. In the flame **SiO_2** remains undissolved and floats in the bead. If a small fragment of glass or other silicate be used, the bases are dissolved in the bead and the insoluble **SiO_2** retains the shape of the fragment, forming a **silica skeleton** in the transparent microcosmic bead.

5. The filtrate, having been freed by evaporation from the excess of **HCl**, contains sodium chloride. This may be used to show the **Na** reactions. Besides the yellow flame color, the following may be tried. Place some of the solution on a watchglass, ascertain that it is neutral (by testpaper), and add some freshly prepared solution of **acid potassium pyro-antimonate,** $K_2H_2Sb_2O_7$ **;** this, at first, produces only a turbidity, but on rubbing the watchglass with a stirring-rod, a white crystalline precipitate of **acid sodium pyro-antimonate,** $Na_2H_2Sb_2O_7$, deposits upon the rubbed parts. The reaction is only applicable when free acids or any substances capable of precipitating antimony are absent. Large quantities of potassium salts also interfere. In very dilute solutions no precipitate falls.

XXXVI. POTASSIUM ACID OXALATE. $KHC_2O_4 + H_2O$.

Salt of sorrel.

1. On heating in glasstube H_2O is at first given off. The salt then blackens and evolves **carbon monoxide gas,** CO, which burns with blue flame. The residue contains K_2CO_3, which is identified by its alkaline reaction and its effervescence with acids. (Compare II., 3 and 4.)

2. **Potassium acid oxalate,** mixed with **manganese dioxide,** MnO_2 and dilute H_2SO_4, will effervesce from the formation and escape of CO_2, detected by $Ca(OH)_2$.

3. When heated with concentrated H_2SO_4 alone, KHC_2O_4 is decomposed, $KHSO_4$ is formed and a mixture of CO and CO_2 gas escapes, which are recognized as above, if a sufficient quantity is used.

4. From its aqueous solution $CaCl_2$ precipitates white **calcium oxalate,** CaC_2O_4, insoluble in acetic acid (see X., 10), soluble in HCl and in HNO_3.

5. **Lead acetate,** $Pb(C_2H_3O_2)_2$, precipitates white **lead oxalate,** PbC_2O_4, soluble in HNO_3.

6. $BaCl_2$ precipitates white **barium oxalate,** soluble in acetic acid, HNO_3 and HCl. Also in aqueous solution of NH_4Cl.

7. $AgNO_3$ precipitates white **silver oxalate,** $Ag_2C_2O_4$, insoluble in dilute HNO_3, soluble in concentrated hot HNO_3 and in $(NH_4.OH)$.

For potassium reactions see IV.

XXXVII. SODIUM HYPOSULPHITE. $Na_2S_2O_3 + 5H_2O$.

Sodium thiosulphate.

1. On heating in the glasstube **H_2O** is given off. Higher heat decomposes the salt into **Na_2SO_4** and **sodium pentasulphide, Na_2S_5**. **$4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S_5$**.

2. After cooling **H_2O** is added to the residue in the glasstube: in a part of this solution the sulphuric acid is recognized by **$BaCl_2$**. The **alkaline sulphide** shows the following reactions:

3. To another part of the solution of the residue from heated **$Na_2S_2O_3$** add **HCl: Na_2S_5** is decomposed and **H_2S** escapes, recognized by its odor and by blackening a strip of paper moistened with lead acetate and held over the testtube.

4. In another part of the solution **$AgNO_3$** precipitates black **Ag_2S**.

5. In another part of the solution **sodium nitro-prusside, $Na_2Fe(NO)C_5N_5$**, produces the beautiful changeable purple color characteristic of alkaline sulphides.

REACTIONS OF HYPOSULPHITES.

6. In the aqueous solution of the unchanged **$Na_2S_2O_3$** the addition of **HCl** produces a yellow precipitate of **S**, while **sulphur dioxide** gas, **SO_2**, escapes, recognized by its odor. Heat accelerates the reaction.

7. **$Pb(C_2H_3O_2)_2$** precipitates white **lead hyposulphite, PbS_2O_3**, which is decomposed on boiling, forming black **PbS** and **H_2SO_4**. **$PbS_2O_3 + H_2O = PbS + H_2SO_4$**.

8. **$BaCl_2$**: white precipitate of **barium hyposulphite, BaS_2O_3**, soluble in much water.

9. **Ferric chloride, Fe'''_2Cl_6**, produces a transient violet coloration, due to the formation of **ferric hyposulphite, $Fe'''_2(S_2O_3)_3$**, which on standing decomposes into **ferrous tetrathionate, FeS_4O_6**, and **ferrous hypo-sulphite, FeS_2O_3**.

XXXVIII. POTASSIUM IODIDE. KI.

1. The white salt generally occurs in cubic crystals. It melts on platinum foil without decomposition. In water it dissolves freely; from this solution:

2. $AgNO_3$ precipitates yellow **argentic iodide, AgI,** insoluble in HNO_3. In NH_4OH the precipitate does scarcely dissolve, but assumes a brighter yellow color from absorption of ammonia. Light decomposes **AgI** and reduces it to **argentous iodide,** Ag_4I_2, and finally to metallic **Ag,** while **I** is liberated.

3. When to a small quantity of **KI** solution $Hg_2(NO_3)_2$ is added in excess, greenish yellow **mercurous iodide,** Hg_2I_2, is precipitated. When a few drops of mercurous nitrate are added to much **KI,** then only gray metallic mercury precipitates, while **mercuric potassium iodide** remains in solution.

4. $HgCl_2$ in slight excess precipitates red **mercuric iodide,** HgI_2, soluble in **KI** and in much $HgCl_2$. (See XXIX., 16.)

5. Acidulate the solution of **KI** with a few drops of H_2SO_4, add **starchpaste** and then, drop by drop, a solution of **potassium nitrite,** KNO_2; iodine is liberated and colors the starch deep blue. $2KI+2H_2SO_4+2KNO_2=2I+2NO+2K_2SO_4+2H_2O$.

6. To the solution add $K_2Cr_2O_7$ and H_2SO_4. Iodine is liberated and, on boiling, escapes as violet vapor. $6KI+K_2Cr_2O_7+7H_2SO_4=6I+K_2SO_4.Cr'''_2(SO_4)_3+3K_2SO_4+7H_2O$.

7. Add to **KI** solution Fe_2Cl_6 and boil. Violet fumes of free iodine escape. $Fe_2Cl_6+2KI=2I+2FeCl_2+2KCl$.

8. To **KI** solution add about 1 cubic centimeter of **chloroform,** $CHCl_3$, and then **chlorine water.** The chlorine will form **KCl** and liberate **I.** On shaking the liquid, **I** dissolves in the chloroform with beautiful magenta color. Large excess of chlorine again discharges the color from the formation of **iodine trichloride,** ICl_3.

9. **Pure, dilute** HNO_3 does not liberate iodine from **KI,** but when it is concentrated, or when it contains nitrous acid it readily sets **I** free.

10. **Palladious chloride,** $PdCl_2$, precipitates, even from very dilute solutions of **KI,** a brownish black **palladious iodide,** PdI_2.

11. **Lead acetate** precipitates yellow **lead iodide,** PbI_2, soluble in much boiling water. On cooling it separates in shining crystals.

12. To show the **potassium** reactions, iodine must be removed by heating **KI** with H_2SO_4 in a porcelain dish. Iodine vapors escape and $KHSO_4$ remains. (See IV.)

XXXIX. POTASSIUM BROMIDE. KBr.

1. Heated on platinum foil **KBr** decrepitates and melts. It is quite soluble in **H_2O**; from this solution:

2. **$AgNO_3$** precipitates yellowish-white **argentic bromide, AgBr,** insoluble in **HNO_3**, difficultly soluble in **NH_4OH**. Light decomposes and darkens **AgBr** in similar manner as **AgCl** or **AgI.**

3. **Mercurous nitrate, $Hg_2(NO_3)_2$**, precipitates yellowish-white **Hg_2Br_2**.

4. A concentrated solution of **mercuric chloride, $HgCl_2$** precipitates from **KBr white mercuric bromide, $HgBr_2$**, soluble in much water.

5. Add **chlorine water** to a solution of **KBr;** bromine will be set free, coloring the liquid yellow. Starch paste added to the liquid will be colored yellow. If the solution containing free **Br** be shaken with **ether** or **chloroform,** they will dissolve **Br** and become colored yellow, the **ether** forming a yellow layer on top, the **chloroform** at the bottom. When **Cl** is used in excess, the color disappears.

6. **Nitric acid,** free from nitrous acid, liberates **Br** from **KBr** when heated, unless the dilution is very great.

7. **Palladious chloride, $PdCl_2$**, does not precipitate **KBr.**

8. **Br** may be shown, when **I** is present, as follows: To a small quantity of the solution of mixed iodide and bromide add some **H_2SO_4**, then **starch paste.** Next add cautiously a few drops of **red fuming nitric acid.** Iodine will be set free first, and color the starch dark blue. **Chlorine water** is then added until the blue color disappears and then drop by drop to liberate **Br,** which may be shaken out with **ether** or **chloroform.**

9. To show the reactions of **K,** the salt is converted into sulphate (XXXIII. 11.)

XL. STRONTIUM SULPHATE. $SrSO_4$.

Celestine.

1. No change by heating on platinum foil.

2. Mixed with dry **Na_2CO_3** and heated on charcoal in the reduction flame, it yields hepar.

3. Neither **H_2O** nor acids dissolve it. When, after digesting

it with distilled water or acids in a clean testtube, a drop of the liquid is evaporated on platinum foil, it leaves no residue, showing that nothing has been dissolved.

4. Finely powdered strontium sulphate is boiled with solution of Na_2CO_3 and filtered while boiling hot. The residue will contain **strontium carbonate, $SrCO_3$,** while the filtrate contains **sodium sulphate, Na_2SO_4.** In the filtrate the sulphuric acid is easily detected by $BaCl_2$. Before pouring the boiling hot solution on the filter, the funnel should be gradually warmed, so as to protect it from cracking.

5. In the residue $SrCO_3$ may be dissolved by **HCl,** forming **strontium chloride, $SrCl_2$,** which is filtered off and tested by flame test (spectroscope) and by precipitants according to XII.

6. A mixture of 2 parts **potassium carbonate, K_2CO_3,** with 1 part **potassium sulphate, K_2SO_4** is boiled with finely powdered $SrSO_4$ and filtered boiling hot. The residue, after washing with water, is dissolved in **HCl** and the solution evaporated to dryness. The residue, $SrCl_2$, colors the flame red and shows the **Sr** reactions.

XLI. BARIUM SULPHATE. $BaSO_4$.

1. No change occurs on heating.

2. It gives hepar when heated with Na_2CO_3 on charcoal in the reduction flame.

3. Neither water nor acids dissolve it.

4. Finely powdered $BaSO_4$ is boiled with solution of Na_2CO_3 and filtered while hot, taking care to preserve the funnel. The residue must be repeatedly boiled with new quantities of Na_2CO_3. The filtrate will contain the sulphuric acid as Na_2SO_4, which is easily detected by the method already known.

5. The residue on the filter contains **barium carbonate, $BaCO_3$,** which is insoluble in water, but readily soluble in **HCl.** It is first washed with some H_2O, the washing rejected and then some dilute **HCl**, is poured upon the residue, which dissolves the $BaCO_3$ forming $BaCl_2$, while any $BaSO_4$ that has not been decomposed, remains on the filter.

6. With the filtrate the **Ba** reactions are made by $CaSO_4$, $K_2Cr_2O_7$ and the green colored flame, (spectroscope) according to XI.

7. The mixture of **K_2CO_3** and **K_2SO_4** (See XL. 6.) is without effect on **$BaSO_4$**. The residue is not dissolved by **HCl**.

XLII. POTASSIUM CYANIDE. KCN.

To the aqueous solution add **HCl : hydrocyanic acid gas** is liberated, recognized by the odor of bitter almonds. Care must be taken to use only a small quantity of **KCN** and not to inhale too much, as the gas is very poisonous.

2. To a small quantity of **KCN** solution add **$AgNO_3$** until a permanent precipitate forms. Divide this into 3 parts. To one add **KCN**, the precipitate redissolves. To another add **NH_4OH**, which also dissolves the precipitate. To the 3d add **HNO_3** which does not dissolve it.

3. To **KCN** solution add some **Fe_2Cl_6** and **$FeSO_4$**, then **NaOH** until a precipitate falls, then heat. The addition of **HCl** dissolves the oxides of iron and a deep blue residue of **ferric ferrocyanide** (prussian blue), **$Fe_3''(CN)_6.Fe'''_4(CN)_{12}$**, remains.

$$6KCN + Fe''SO_4 = K_4Fe''(CN)_6 + K_2SO_4.$$

$$3[K_4Fe''(CN)_6] + 2Fe'''_2Cl_6 = Fe''_3(CN)_6.Fe'''_4(CN)_{12} + 12KCl.$$

4. This precipitate of prussian blue is filtered off and washed, then rinsed from the filter into a test tube and **NaOH** added. **Ferric hydrate $Fe_2(OH)_6$** separates, and **sodium ferro-cyanide, $Na_4Fe(CN)_6$** remains in solution. On acidulation with **HCl**, prussian blue is again formed.

$$Fe''_3(CN)_6.Fe'''_4(CN)_{12} + 12NaOH = 2[Fe_2(OH)_6] + 3[Na_4Fe(CN)_6].$$

$$3[Na_4Fe(CN)_6] + 2[Fe'''_2(OH)_6] + 12HCl = Fe''_3(CN)_6.Fe'''_4(CN)_{12} + 12NaCl + 12H_2O.$$

5. To **KCN** solution add **yellow ammonium sulphide, $(NH_4)_2S$** and evaporate at gentle heat, (in water bath.) The residue contains **potassium sulphocyanide** (rhodanate), **KCNS.**

$$KCN + (NH_4)_2S_2 = KCNS + (NH_4)_2S.$$

This is dissolved in water and **Fe_2Cl_6** added, which produces a deep red solution of **ferric sulphocyanide $Fe'''_2(CNS)_6$.** XVIII. 17.

XLII. LITHIUM CARBONATE, L_2CO_3.

1. **Lithium carbonate** is sparingly soluble in water and shows the alkaline reaction with test papers. (See II. 3.)

2. With **HCl** it effervesces, giving off **CO_2**, while **lithium chloride, LiCl,** is formed.

3. Addition of strong alcohol and ether does not render the **LiCl** solution turbid.

4. **Na_2HPO_4**, precipitates white **lithium phosphate,** little soluble in water, **$2Li_3PO_4+H_2O$**.

5. The flame is colored crimson by lithium salts, similar to that of strontium, from which it is most easily distinguished by the spectroscope.

XLIV. COMMERCIAL SULPHURIC ACID, H_2SO_4.

Oil of Vitriol.

The reactions of sulphuric acid in dilution, or in combination, have already been studied. (III.) Some, peculiar to the concentrated, raw acid of commerce, are important enough to deserve attention.

1. When a clean splinter of wood is touched with a drop of oil of vitriol, the spot blackens and becomes charred, the acid combines with the water of the wood and leaves the carbon.

2. Pour a little acid upon some cane sugar, it will be charred in like manner. Even small quantities of **H_2SO_4** diluted with much water may be detected by the blackening of cane sugar when carefully heated together in a water bath.

2. Pour some acid upon a piece of cloth mixed of cotton and wool; after a minute wash with much water, the **cotton fibre** is destroyed and the wool but little affected.

4. When a few drops of **H_2SO_4** are added to about double its volume of water, the mixture becomes hot.

Care must be taken in making mixtures on a larger scale, on account of this heating. The acid must be cautiously and gradually added to the water, and time be given to cool, before new quantities are added.

5. When commercial sulphuric acid is poured into much water, **lead sulphate, $PbSO_4$,** which is dissolved in the concentrated acid, is precipitated, being insoluble in the dilute acid. (See XXV, 5.)

XLV. GOLD CHLORIDE. $AuCl_3$.

1. Gold is insoluble in either hydrochloric or in nitric acid, but readily dissolves in a mixture of the two, forming **aurochloric acid, $AuCl_3$, $HCl+3H_2O$.** The solution of this salt in water has, even in dilution, an intense yellow color.

2. From the acidulated cold solution H_2S precipitates black **auric sulphide, Au_2S_3,** from boiling solutions, brown **aurous sulphide, Au_2S.** These precipitates are insoluble in **HCl** or in **HNO_3**, but are decomposed by hot nitro-hydrochloric acid. Colorless **ammonium sulphide $(NH_4)_2S$** does not dissolve them, but in **yellow ammonium sulphide $(NH_4)_2S_2$** or in **yellow sodium sulphide, Na_2S_2,** they readily dissolve, forming ammonium (or sodium) **sulph-aurate, $(NH_4)_3AuS_3$.**

4. **Stannous chloride, $SnCl_2$,** containing a little **stannic chloride, $SnCl_4$,** produces even in very dilute solutions a purple called **purple of Cassius**. (See XXXI. 16.)

4. **Ferrous sulphate, $FeSO_4$,** precipitates **metallic gold** as a fine powder, which by reflected light looks brown to yellow and in transmitted light green to blue. By separating the powder and rubbing it in an agate mortar, the metallic lustre is developed.

5. Many other reagents reduce gold in a similar manner, among them oxalic, sulphurous and arsenous acids, potassium nitrite, alkaline tannates, etc.

SYSTEMATIC EXAMINATION OF SUBSTANCES CONTAINING ONLY A SINGLE BASE.*

Dissolve the substance (if not already in liquid form) either in water, or if this does not succeed, **HCl** or in **HNO_3**. If the solution is made in water or the specimen is furnished in the liquid state, a small amount of **HCl** must be added, so as to give an acid reaction.

Sulphuretted hydrogen is added in some quantity. It either produces a colored precipitate of a metallic sulphide, or a white one of pure **S** or fails to precipitate anything.

I. A colored precipitate is formed by H_2S.

This indicates that the solution may contain **Ag, As, Au, Bi, Cd, Cu, Hg, Pb,** or **Sn.** Observe the color of the precipitate. It may be:

a. Black or brownish black.

This indicates the presence of either:

Ag, Au, Bi, Cu, Hg, or **Pb.**

To recognize which of these is present, dilute a portion of the original solution with much water and add **HCl**. If this produces a white precipitate, it may consist either of **AgCl** or of **Hg_2Cl_2.** (**$PbCl_2$** remains in solution, being soluble in 135 parts of cold water.) Decant the liquid from the precipitate and add **NH_4OH**. This dissolves the precipitate of **AgCl,** but changes the color of **Hg_2Cl_2** to black and leaves it undissolved. Verify for **Ag** by reprecipitating **AgCl** from the ammoniacal solution with **HNO_3**; for **Hg** by testing the original solution on bright copper foil. If no precipitate was thrown down by **HCl**, there may be present:

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* Before the student enters on the analysis of more complicated substances, specimens may be given him, which dissolve readily in water or hydrochloric or nitric acid, and which, while unknown to him, contain one of the base selected from one of the foregoing examples, whose reactions are now familiar to him. The systematic examination according to this short course will serve as a recapitulation and prepare him for the more comprehensive examination that follows. When a base is detected, it should be verified by some of the reactions given in the preceeding examples.

Au, Bi, Cu, Hg, (as mercuric salt) or **Pb**. To a new portion of the original solution, add **H_2SO_4** and some alcohol. A white precipitate of **$PbSO_4$** will fall if lead be present.

To a new specimen of original solution add **NH_4OH** drop by drop. The precipitate may be blue, white or orange.

A **blue** precipitate, redissolved by excess of **NH_4OH** to a deep blue solution, indicates copper. Verify in the original solution by ferrocyanide of potassium and by bright iron.

A **white** precipitate may indicate **Bi** or **Hg** (mercuric). Separate the precipitate by filtering or decanting, mix with a little **S** and **KI** and test on charcoal before the blowpipe.

A **scarlet** incrustation, surrounding the heated spot, indicates **Bi**. Confirm by adding original solution to much water, and by potassium chromate.

A **yellowish brown** incrustation indicates **Hg**; confirm by **NaOH** giving yellow precipitate of **HgO**; also by **KI** and by copper foil.

An **orange** precipitate, produced in the original solution by ammonia water indicates **Au**. Verify by the addition of stannous chloride, (containing some stannic chloride) to the original solution. Purple of Cassius will be formed if gold be present. Test also by reducing the gold to metallic state by oxalic acid or by ferrous sulphate.

b. BROWN.

This indicates **Tin**. The brown stannous sulphide, **SnS**, disolves in yellow ammonium sulphide, from which it is reprecipitated by **HCl** as yellow stannic sulphide, **SnS_2**. Verify by **$AuCl_3$**.

c. ORANGE.

This indicates **Sb**. The orange **Sb_2S_3** dissolves in ammonium sulphide and is reprecipitated by dilute acids. Confirm by reducing **Sb** from original solution by **Zn** on platinum foil.

d. YELLOW.

This may indicate either

As, Cd, or **Sn** (**SnS_2**).

To recognize which of these is present add ammonium sulphide.

If there is no solution the yellow precipitate consists of **CdS**.

If it disolves there may be arsenic or a stannic salt. To another portion of the yellow precipitate by hydrogen sulphide add ammonium carbonate. If solution occurs, **As** is present, verified by garlic odor, reduction by charcoal in glass-tube and by other confirmatory tests.

If no solution is affected by ammonium carbonate the yellow precipitate consists of **SnS_2**.

II. A white precipitate is formed by H_2S.

This consists of reduced sulphur in a state of fine subdivision. It may be tested by collecting it and heating it in a glass-tube, when it will melt, sublime, form brownish drops, which become yellow on cooling, burn in air and give the odor of **SO_2**. The precipitation of **S** accompanies the reduction of higher oxides to lower, the decomposition of acids containing much oxygen, or indicates the presence of chlorine and similar substances. In connection with a change in color of the original solution, it therefore may indicate the presence of ferric salts, of chromates, permanganates, chlorates etc. It is not regarded as a conclusive reaction, and therefore disregarded at this part of the course.

III. No precipitate by H_2S from acid solution.

NH_4Cl and **NH_4OH** are successively added (no attention is paid to any precipitate produced by them), and then **$(NH_4)_2S$**. This may form a colored or a white precipitate, or fail to affect the solution. A precipitate may indicate:

Al, Ba, Ca, Co, Cr, Fe, Mg, Mn, Ni, Sr, Zn. Of these **Co, Fe, Mn, Ni** and **Zn** is precipitated as **sulphide; Al** and **Cr** as **hydrate**, the rest only when present as phosphate, borate, oxalate, tartrate or citrate. According to color the precipitates are distinguished:

a. BLACK PRECIPITATE.

This may contain **FeS, CoS** or **NiS**. (As **NiS** is not entirely insoluble, the black precipitate, when brought on a filter, stains the paper brown.)

To distinguish these, the original solution is tested with potassium ferro-cyanide: a dark blue precipitate indicates a ferric salt; verified by **KCNS.**

A pale blue precipitate, turning darker blue in contact with air, indicates a ferrous salt; verified by red potassium ferricyanide. A greenish precipitate may indicate **Co** or **Ni.** The original solution containing **Co** has a red, that containing **Ni** a green color. **NaOH** precipitates **Ni** as green, **Co** as blue hydrate. Verified by the microcosmic bead colored with **Co** having blue color. The bead with **Ni** is red, while hot, yellow after cooling.

b. FLESH COLORED PRECIPITATE.

Consists of **MnS.** Mix this with KNO_3 and Na_2CO_3 and heat upon platinum foil. It will fuse and form a bluish-green mass of manganate.

c. GREEN PRECIPITATE.

Consists of $Cr_2(OH)_6$. When this is mixed with KNO_3, and heated on platinum foil, yellow potassium chromate will be formed.

d. WHITE PPRECIPITATE.

This may consist of $ZnS, Al_2(OH)_6$, or of phosphate, oxalate, tartrate, citrate or borate of an alkaline earth.

To the original solution add **NaOH,** carefully, drop by drop. This at first precipitates all the above; when added in excess, it redissolves **Zn** and **Al** but leaves the others undissolved.

Zinc and aluminium are readily recognized by transferring the precipitate obtained with $(NH_4)_2S$ to charcoal and heating before the blow-pipe, adding cobaltous nitrate. A blue opaque mass indicates **Al,** a green mass **Zn.**

If neither **Zn** nor **Al** are found, the salts of the alkaline earths must be sought for in the precipitate by $(NH_4)_2S$, or in the residue left undissolved by **NaOH.**

The white precipitate is decanted, and H_2SO_4 added. This converts **Ba, Sr,** or **Ca** into difficultly soluble sulphate, while $MgSO_4$ dissolves.

The insoluble sulphate is repeatedly boiled with Na_2CO_3 and water, and filtered while hot. **Ba, Sr** or **Ca** is thereby converted into a carbonate, which readily dissolves in **HCl** and admits of examination according to IV.

IV. No precipitate by H_2S or by $(NH_4)_2S$.

Add to the original solution (or that obtained above.) NH_4Cl

and **NH_4OH** and lastly $(NH_4)_2CO_3$. A white precipitate indicates **Ba, Sr** or **Ca**; if no precipitate falls **Mg, K, Na, Li** and **NH_4** must be looked for. If a precipitate is formed, add to original solution **$K_2Cr_2O_7$**: a yellow precipitate indicates barium; confirm by flame color. If **$K_2Cr_2O_7$** does not form a precipitate, add **H_2SO_4**, a precipitate, falling slowly, indicates strontium; confirm by flame test. If neither of the two preceding reagents produces a precipitate, add ammonium oxalate: a white precipitate indicates **Ca**.

V. No precipitate by H_2S, by $(NH_4)_2S$, nor by $(NH_4)_2CO_3$ in presence of NH_4Cl and NH_4OH.

To the original solution add **NH_4Cl** and **NH_4OH**, then **Na_2HPO_4**: a white precipitate indicates **Mg**. If **Mg** is present as a phosphate, it will be precipitated before the addition of sodium phosphate.

VI.

When a negative result has been obtained by all the preceding reagents, only alkalies can remain.

The presence of ammonium is ascertained by adding **NaOH** to the original solution and heating: **NH_3** is given off, which shows alkaline reaction with moistened testpaper held into the fumes. It may also be recognized by its odor, or by giving white fumes with **HCl**.

If ammonium be absent, apply the flame tests to the original solution. (If this be too dilute, it must be concentrated by evaporation.) The platinum wire used should be scrupulously clean, and must be held into the flame until all color disappears, before it is dipped into the solution to be tested. It is then held into the lower, outer portion of the non-luminous flame, which becomes colored as follows:

A **yellow** color shows the presence of **Na**.

A **violet** color indicates **K**. Confirm in the original solution by sodio-cobaltic nitrite, or by platinum chloride, or by sodium acid tartrate; also by the spectroscope.

A **crimson** color indicates **Li**, to be confirmed by the spectroscope.

SYSTEMATIC COURSE OF QUALITATIVE ANALYSIS.

A. PRELIMINARY EXAMINATION.

I. Heating in glass-tube.*

If the substance, to be tested, is a liquid, it is first examined with test papers, then a portion of it is evaporated, and the residue (if any remain) is subjected to the preliminary examination. A portion of the **solid** substance is heated in the glass-tube and the following appearances noted:

1. **H_2O** is given off. Test this with litmus paper, whether it be **neutral** (water of crystallization), **alkaline** (**NH_3**), or **acid** (**SO_2,HCl,...**).

2. A **sublimate** forms.

Red-brown drops, congealing to yellow solid, indicate **S.**

A **white** sublimate indicates ammonium salts, **$HgCl_2$, Hg_2Cl_2, As_2O_3, Sb_2O_3.**

A **yellow** sublimate: **HgI_2** (becomes red on rubbing with a glass-rod), **As_2S_3**, (soluble in ammonium carbonate solution.)

A **black** sublimate: **HgS,** becomes red by rubbing with a glass-rod.

Metallic mirror: As.

Gray globules: Hg.

3. **Gas** is given off either colorless or colored.

a. COLORLESS.

Oxygen indicates peroxides, chlorates nitrates, permanganates, etc.

CO: oxalates.

CO_2: carbonate (the gas renders baryta water turbid.)

NH_3: ammonia compounds.

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* Glass-tubes for heating solids for these and similar tests should be of hard infusible glass, about 10 centimeters long and 6 millimeters in width, and must be clean and dry.

SO_2: sulphurous acid, etc., known by odor and acid reaction.

H_2S : blackens moist lead paper; odor.

Cyanogen : smells of bitter almonds and burns with peach bloom colored flame.

NO_2, red gas, indicates nitrates.

b. COLORED.

Chlorine, green.

Iodine, violet.

Bromine, yellowish brown.

Nitrogen tetroxide, red-brown.

4. **The substance melts :** Alkali salts.....

5. The substance does does not melt, but **changes color** by heating.

A **white** substance turning **yellow,** when heated, and becoming white again by cooling, **ZnO.**

White, changing to **deep yellow,** when hot, becoming pale yellow, when cool: **SnO_2**.

White or **yellow,** turning **dark-yellow** on heating, **fusing** and then turning pale yellow on cooling: **Bi_2O_3**.

White or **yellow,** changing to **dark-red** on heating, **fusing,** then yellow on cooling: **PbO.**

Red changing to **black,** returning to red on cooling: **HgO** (volatile,) **Fe_2O_3** (not volatile.)

Red changing to **yellow : HgI_2**.

6. The substance **blackens : organic** compounds.

7. The substance remains **unchanged : $BaCO_3$, $BaSO_4$**,...

II. Blowpipe tests on Charcoal.

1. **Deflagration :** chlorates, nitrates.

2. The substance melts, is absorbed by the charcoal, or forms transparent glass: alkali salts. The residue reacts alkaline (carbonates, nitrates, oxalates, tartrates etc.)

3. The substance is infusible: earths, **SiO_2, Zn O.**

4. The substance, on being ignited, shows bright luminosity: **ZnO.SrO, MgO, CaO.**

If an odor is developed during these tests it may indicate **As** (garlic), **SO_2, NH_3**.

III. Blowpipe tests on charcoal after addition of sodium carbonate.

1. **Hepar** is formed by all compounds of **S** if heated long enough in the full reduction flame.

2. A **gray metallic powder** is formed without incrustation of the charcoal; if it is attracted by magnet, it may be **Fe, Ni** or **Co;** otherwise **Mo** or **Pt** or **W.** (The reduction of tungstic acid however only succeeds, when small quantities of soda are employed.)

3. **A metallic globule, without incrustation.**

Red globule, Cu (blowpipe flame colored greenish).

White: 1. **Ag** (sometimes with small dark incrustation).
2. **Sn,**. reduction facilitated by **KCN** or borax. Long heating oxidizes the globule to **SnO_2**, not volatile, yellow while hot, white when cool.

Yellow: Au.

4. **A metallic globule accompanied by incrustation.**

a. The globule is **ductile,** the incrustation **yellow: Pb.** When the reduction flame is directed upon the incrustation it volatilizes, coloring the flame blue.

b. The globule is **brittle.** A **white** incrustation indicates **Sb;** this volatilizes in the oxidation flame with greenish color. A **yellow** incrustation, darker while hot, indicates **Bi,** it is of a brighter yellow than that of **Pb**, volatile in the reduction flame, but imparting no color to it. If to the substance containing **Bi** a little **KI** and **S** is added and the mixture heated, a scarlet incrustation will be produced.

5. **Incrustation without metallic globule.**

White: As (odor of garlic) very volatile; disappears on heating with blue flame color.

White, and **yellow** while hot: **Zn,** disappears in reduction flame, but not in oxidation flame.

Red brown: Cd, best seen when cool.

IV. Color of beads of microcosmic salt or borax.*

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* Instruction for forming beads has already been given on page 5. The lamps must be tilted so as to prevent the melted salt from falling into the tube. Phosphate of sodium, ammonium and hydrogen, usually called *microcosmic salt* is more fusible and therefore harder to manage, but deserves preference in many cases, especially for experiments in the reduction flame, which it shows much more perfectly than when borax is used. The following table specifies only the microcosmic salt reactions, from which those made from borax do not very materially differ.

COLOR OF MICROCOSMIC BEAD.

	OXIDATION FLAME.			REDUCTION FLAME.		
Color	Hot	Cold	Remarks	Hot	Cold	Remarks
Colorless	Ba	Ba	turbid if super saturated.	Ba	Ba	turbid if super saturated.
	Sr	Sr		Sr	Sr	
	Ca	Ca		Ca	Ca	
	Mg	Mg		Mg	Mg	
	Al	Al		Al	Al	
	Earths	Earths		Earths	Earths	
	Sn	Sn		Sn	Sn	
	Ta	Ta	when feebly saturated.	Ce	Ce	
	Nb	Nb		Di	Di	
	Fe	Fe		Mn	Mn	
	Ni	Ni				
	Sb	Sb				
		Pb				
		Bi				
		Cd				
		Ti				
Green	Cr	Cr		Cr	Cr	
		Ur		Ur	Ur	
	Cu				V	
	Mo	Mo		Mo	Mo	
				Fe		str. satur.
Blue	Co	Co		Co	Co	
		Cu			W	with Fe red
					Nb	str. satur.
Yellow	Ag	Ag	opal str. satur.			
	Bi		cold: colorless			
	Ur		cold: green			
	Pb		cold: colorless			
	Cd		cold: colorless			
	Ti		cold: colorless	Ti		cold:violet
		Fe	strongly satur.			
		Ni	strongly satur.	Ni	Ni	
Red	Fe		fading while cooling.		Cu	opaque red with tinfoil
	Ni					
Violet	Mn				Ti	after adding tinfoil.
	Di					
Gray reduced metal				Ag	Ag	
				Pb	Pb	
					Bi	after adding tinfoil
				Ni	Ni	
Insoluble skeleton	Si	Si		Si	Si	

The specimen is first tested in the oxidation flame and then in the reduction flame, the reactions being noted in the preceding table. They depend on the conversion of the metallic oxides into borates, in case of **borax, $Na_2B_4O_7$,** being used. When **microcosmic salt, $Na.NH_4.H.PO_4$,** is used, the heat expels **$NH_4.OH$** and **sodium metaphosphate, $NaPO_3$,** remains, in which the metallic oxides dissolve.

V. Coloration of flame.

As the chlorides are generally more volatile than other salts, **HCl** is added to the specimen, if it does not color the flame well without such addition. The specimen is attached to the loop of a clean platinum wire, if a solid, by heating the wire and then holding it to the specimen, which melts and adheres to the wire. If this does not succeed, the substance is attached by means of a little distilled water. When liquids are to be examined, the wire, bent into a loop, is strongly heated and plunged into the liquid, when generally enough adheres to show the flame reaction. The wire must be scrupulously clean and should be heated in the nonluminous flame until all the color disappears, before the specimen to be tested is attached. The nonluminous flame of the Bunsen lamp or of an alcohol lamp or the blow pipe flame are colored:

Yellow by **Na.**

Red by **Sr, Li, Ca** (orange red).

Green by **Ba** (yellowish), **Tl,** many salts of **Cu, boracic,** and **phosphoric Acid.**

Blue by **$CuCl_2$** and **In.**

Violet by **K.**

When **Na** is present with other substances, its yellow rays may be quenched, by viewing the flame through cobaltglass or indigo solution: then the color of **K** or **Li** or **Sr** may be distinctly seen.

Viewed through green glass the yellowish-green flame of **Ba** appears blueish-green, **Ca** a pure green (parrot-color), while **Sr** appears faint yellow.

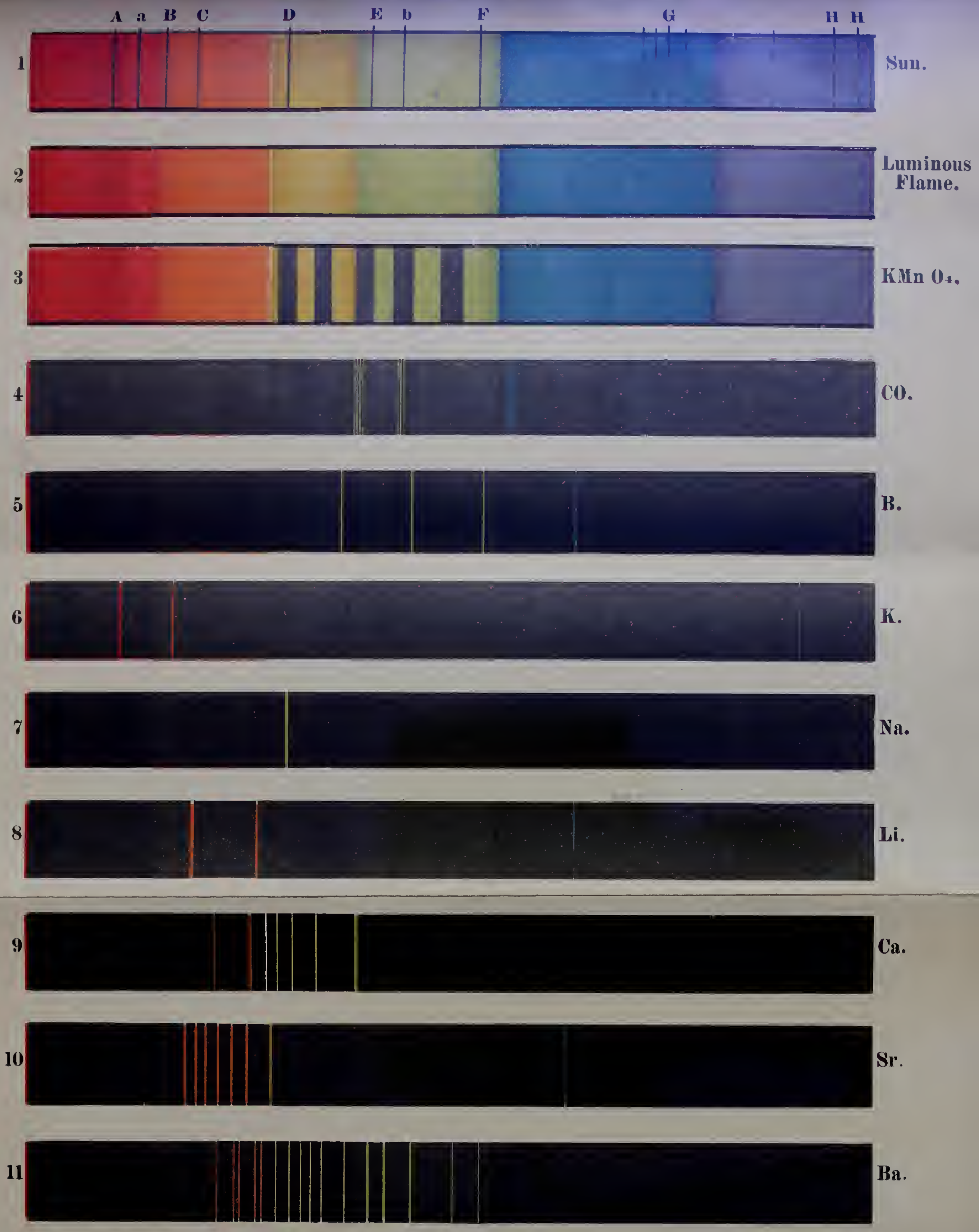
VI. Use of the Spectroscope.

For the ordinary purposes of analysis small direct vision spectroscopes are quite sufficient. Their price is so low as to bring them in reach of every analyst. They consist of a cylindrical tube, containing 5 prisms, a drawtube with adjustable slit, and a lens placed between them, to render the rays parallel.

To use the instrument, it is first directed toward the sky and the draw-tube and slit so adjusted, that the dark lines, mapped in No. 1 of the table (spectrum of the sun) may appear sharp and distinct. These lines are called **Fraunhofer's** lines and some of the more prominent are distinguished by letters of the alphabet. They represent vapors of various elements in the solar atmosphere. The instrument is then directed towards the luminous flame of the Bunsen lamp which will show the colors of the spectrum without the dark lines, (table No. 2.) and secured in its position, so as to have the slit about 5 or 6 inches (125 to 150 Mm.) distant from the flame.

When thus arranged, glass-tubes containing colored solutions may be held near the slit, between it and the flame. Parts of the color spectrum are thereby shaded out, while other parts show brightly (absorption spectra). Many substances, of very similar colors, may thus be readily distinguished from each other by the different position of the absorption bands. The absorption spectrum of a dilute solution of **potassium permanganate** is figured in No. 3. of the table. There are five distinct black bands in the yellow and green, when a dilute solution is used. With greater concentration the bands widen and and finally coalesce.

When the airholes of the Bunsen burner are opened, so as to render the flame nonluminous, no light appears, until the instrument is directed towards the base of the flame, when 4 groups of fine lines, (almost coalescing into faint broad lines, when viewed by a small instrument) appear as shown in No. 5. of the table. They form the spectrum of carbon monoxide, and are everywhere present in the flame, but show best towards its base. They should be well known, lest they be mistaken for lines produced by other vapors, especially for the spectrum of boracic acid (No. 5.) to which they bear a slight resemblance. The spectra of colored flames show a less number of lines, at a lower to temperature of the flame, than at the higher one, such as may be produced by the oxyhydrogen burner or by the electric arc. Those mapped in


A a B C D E b F G H H
1
Sun.
2
Luminous Flame.
3
KMn O4.
4
CO.
5
B.
6
K.
7
Na.
8
Li.
9
Ca.
10
Sr.
11
Ba.

the table are the ones generally seen in the Bunsen flame. They are produced by coloring the flame, as directed in the preceding section (V.), and viewing it through the spectroscope.

The spectrum of **K** (No. 6.) is characterized by a bright line in the extreme red; when chlorate of potassium is used, the higher temperature shows another red line and one in the extreme violet.

Sodium (No. 7.) with the smaller instrument shows a single, brilliant, yellow line, which, by more powerful instruments, is resolved into two. As sodium is almost universally present, and as very minute quantities show the line very brightly, it is frequently conjoined to the lines of other spectra and serves as a guide to measure the distance of other lines.

Lithium (No. 8.) shows a red line at ordinary, an orange at higher temperature and an additional blue one at very high heat.

Thallium, a very rare metal, is distinguished by a single green line.

Indium, a still rarer substance, by one line in the blue and another in the violet part of the spectrum.

Rubidium and **Caesium** have spectra with numerous lines, the first, **Rb,** being remarkable for a double red line, **Cs** for a double blue of great brilliancy.

The spectra of the alkaline earths are quite complicated, yet easily recognized by comparison with the table: **Ca,** No. 9. **Sr,** No. 10. **Ba,** No 11.

When several substances are at once placed into the flame, their spectra appear simultaneously, but generally in such manner, that the spectrum of the most volatile substance is brightest at first, and then fades, while the others become brighter and then fade out also according to their volatility.

VII. Solution of the substance.

1. **The substance is solid, but not a metal.** First try to dissolve it in **water.** If the whole, or the greater part is soluble in **H_2O,** treat a larger quantity (1 to 3 grammes) in like manner, and examine the aqueous solution separately. If the substance is insoluble in water, filter off some of the liquid, place a drop or two on clean platinum foil and evaporate, observing whether it leaves a solid, volatile or non-volatile residue (see page 5). If only an insignificant residue remains, the substance

may be considered as insoluble in **H_2O**, and a portion of it is tested with **dilute hydrochloric acid.** Attention must be paid to the evolution of **CO_2, H_2S, SO_2** or **HCN.**

If dilute hydrochloric acid does not dissolve the substance, even at boiling heat, **concentrated HCl** is next tried. (Evolution of chlorine indicates higher oxides, chromic or chloric acid.) Whatever is not dissolved by **HCl,** may be tried with **nitric acid**. Any residue, still remaining undissolved, is treated with **aqua regia** (nitro-muriatic acid, prepared by mixing 2 parts of concentrated hydrochloric acid with 1 part of concentrated nitric acid.)

Substances resisting the action of acids are treated by special processes described further on.

2. **The substance is a liquid.** Its reaction with litmus paper is ascertained, then a portion of it is evaporated to dryness and the residue, if any, is subjected to the preliminary examination.

3. **The substance is a metal.** Treat with nitric acid. This will leave undissolved metallic **Pt** and **Au** (sometimes retaining some **Ag**), and **Sb** and **Sn** as white oxides (sometimes retaining **As**). Be careful not to use too much concentrated nitric acid, lest crystalline precipitates of metallic nitrates form, which are easily soluble in water, but not in concentrated nitric acid. They might be mistaken for **SnO_2** or **Sb_2O_5.** After decantation of the acid these precipitates readily dissolve in hot water. **Au** and **Pt** dissolve in aqua regia. **Sb** and **Sn** are separated by filtration, washed on the filter and then dissolved in hydrochloric acid.

4. Solutions should be obtained as concentrated as possible. Avoid any large excess of acids, especially of **HNO_3,** which impedes the action of **H_2S**. An excess of acid is to be removed by evaporation; but this may occasion loss, as, for instance, during the evaporation of a solution of **As_2O_3** in **HCl**, **$AsCl_3$** is volatilized. In such case **$KClO_3$** or **HNO_3** are added to the solution.

It is generally more appropriate in those cases in which a substance dissolves partly in water and partly in acid, not to mix the solutions, but to examine the aqueous and the acid solutions separately. The **aqueous** solution will contain the **alkalies,** the **nitrates, chlorates,** (**sulphites**) but **none** of the **phosphates** of alkaline earths, which are found in the acid solution. Alkalies are rarely found in the acid solution. The result of the solving action of **HCl** and of **HNO_3** need not be kept separate, provided no precipitate forms on mixing them.

B. DETECTION OF BASES. *

GENERAL BEHAVIOR OF THE METALS WITH THE GROUP-REAGENTS.

H_2S Precipitates from acid solution:		**$(NH_4)_2S$** Precipitates from ammoniacal solution as		**Na_2HPO_4** Precipitates	**Not precipitated** by the preceding reagents.
Precipitate is **soluble** in **$(NH_4)_2S$**.	Precipitate **insoluble** in **$(NH_4)_2S$**	**Sulphides**	**Hydroxides**		
As	**Hg**	**Ni**	**Al**	**Ba**	**K**
Sb	**Ag**	**Co**	**Cr**	**Sr**	**Na**
Sn	**Pb**	**Fe**		**Ca**	**(NH_4)**
	Bi	**Mn**	Be	**Mg**	**Li**
Au	**Cu**	**Zn**	Ta		
Pt	**Cd**		Nb		Cs
Ir		Tl			Rb
Mo	Pd		Ce		
	Os		La		
Se	Rh		Di		
Te	Ru		Y		
			Zr		
(V)			Th		
(W)			Ti		
		Phosphates, oxalates borates and certain other salts of alkaline earths.			
		Ur			
VI.	V.	IV.	III.	II.	I.

The aqueous solution of the substance is acidulated with **HCl**, so as to insure the presence of **free** acid, for some salts, soluble in water, show **acid reaction** with test papers, though they contain **no free** acid, whose presence is necessary for separations by **H_2S** (such as **Zn from Cu**).

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* Neither the term *bases*, nor that of *metals*, which might have been substituted for it, is strictly correct. For, among the substances examined in this course, there are acids formed by metals, and some metalloids.

If solution was effected by means of acids, dilute with water. If a precipitate form, either in the aqueous solution by **HCl** * or in the acid solution by **H_2O,** it may be disregarded for the present, and **sulphuretted hydrogen** is to be added to saturation (best by passing a current of **H_2S** gas through the solution.) The precipitate contains all the metals of groups V and VI.

Separate this precipitate by filtration, supersaturate the filtrate with **NH_4,OH**, disregarding any precipitate. and then add **$(NH_4)_2S$.** The precipitate contains groups III. and IV.

A portion of the filtrate from the precipitate by **$(NH_4)_2S$** is heated to expel surplus of ammonium sulphide and then tested by addition of **NH_4OH** and **Na_2HPO_4**. A white precipitate indicates **alkaline earths,** group II. Treat according to § 7 and 12.

In the filtrate from the precipitate § 12, the **alkalies,** group I, remain.

FIRST GROUP. ALKALIES: K, Na, (NH_4), Li.

§ 1. The liquid, from which the groups II to VI have been removed by the appropriate group-reagents, or from which these groups were originally absent, is evaporated to dryness and the residue ignited to expel ammonium salts. The residue may contain: **K, Na, Li.**

§ 2. A portion of this residue is attached to the loop of a platinum wire, and introduced into the non-luminous Bunsen flame (or the blowpipe flame). The colored flame is examined by the spectroscope, or by other means as follows:

Yellow coloration shows **Na** (see example I. 2, page 15). Examine through blue glass for presence of **K** and **Li.**

Violet color shows **K.**

Red color shows **Li.**

The spectroscope is used according to the preceding directions (preliminary examination VI.) and with the help of the table the alkali metals will be easily identified.

§ 3. **Detection of the alkalies in the wet way.**

As the flame test is so very satisfactory, there is rarely need to resort to this. Separation for qualitative purposes is seldom required. (NH_4) gives many reactions similar to **K** so that it must first be removed by igniting the residue, § 1. This is then dissolved in little water and **$PtCl_4$** and **alcohol** are added. The yellow precipitate, **$2KCl.PtCl_4$**, is separated by filtration, the filtrate evaporated to dryness and from the residue the **sodium** salt is extracted by water. If **iodine** is present, it obscures the reactions, and must be removed by converting the salts into sulphates, (see example XXXVIII. 11.) or else **K** may be precipitated by **tartaric** acid.

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* From neutral or acid solutions **HCl** may precipitate **Ag, Hg, Pb, Tl**; from alkaline solutions either hydrochloric or nitric acid may precipitate, silicic, boracic, antimonic, tungstic, molybdic acid, (benzoic acid), sulphur from hyposulphites and polysulphides, and various basic salts, cyanides, sulphides etc.

Sodio-cobaltic nitrite will precipitate even small quantities of **K** without requiring the removal of the bases of the second group (see example IV. 7.)

For precipitation of **Na** see example XXXVI. 5.

§ 4. **Lithium** may be separated from **K** and **Na** by converting them into chlorides. A mixture of ether and absolute alcohol will dissolve from their mixture only **LiCl**, leaving **KCl** and **NaCl** behind. For reactions of **Li** see example XLIII.

§ 5. **Tests for (NH_4).** A part of the original substance is placed into a porcelain capsule and **NaOH** added: the characteristic odor and the alkaline reaction of **NH_3** gas, the formation of white fumes with a drop of acetic acid or **HCl**, brought near it on a glass rod, detect it easily.

SECOND GROUP. ALKALINE EARTHS: Ca, Ba, Sr, Mg.

§ 6. A small portion of the liquid, from which groups III. to VI. have been removed by **H_2S** and **$(NH_4)_2S$**, or which did not originally contain members of these groups, is treated with **NH_4OH** and then with **Na_2HPO_4**. If a white precipitate is formed, it shows the presence of members of the second group.

§ 7. To some of the balance of the liquid (in a small portion of which sodium phosphate has produced a precipitate) **NH_4Cl** and **NH_4OH** is now added, and then **$(NH_4)_2CO_3$**. The white **precipitate** may contain **Ba**, **Sr** and **Ca**, in the filtrate **Mg** and the **alkalies** (group I.) remain. The precipitate, after washing, is dissolved in **HCl** and contains now the chlorides of **Ba**, **Sr** and **Ca**.

§ 8. To separate these, the liquid is treated with a slight excess of **potassium dichromate, $K_2Cr_2O_7$**, or **potassium chromate, K_2CrO_4**, and acetic acid. A yellow precipitate indicates

Ba; this is removed by filtration and confirmatory reactions made according to example XI.

§ 9. **Sr** may now be separated by addition to the filtrate of **H_2SO_4**, which precipitates **$SrSO_4$**. Or, as strontium chromate is soluble in acids, but not in alkalies, the filtrate may be rendered alkaline by adding **KOH** and then enough **K_2CrO_4** to precipitate all of **Sr.** Filter and examine according to example XII.

§ 10. In the filtrate **Ca** remains. This is precipitated by ammonium oxalate and confirmed by reactions according to example X., 6 and ff.

§ 11. In a small part of the filtrate obtained above § 7, containing **Mg** and alkalies, magnesium is detected by **Na_2HPO_4**, and **NH_4OH.** If it be absent, the rest of the filtrate may be used to test for the alkalies according to § 1. But if **Mg** is present, it must be removed from the solution, not by sodium phosphate, which introduces **Na,** but either by ammonium phosphate or by the following method:

§ 12. The solution § 7, freed as above from **Ba, Sr** and **Ca** is evaporated to dryness and ignited to expel ammonium salts. The residue is dissolved in **H_2O**, and **milk of lime** or **baryta water** (*free from alkalies*) is added to alkaline reaction; boil and filter off the mixture of **magnesium** and **calcium hydrates.** The precipitate is washed, the wash-water and the first filtrate are mixed and concentrated by evaporation, The **Ca** which is yet present is removed by ammonium oxalate, or by **NH_4OH** and **$(NH_4)_2CO_3$.** If baryta was used **H_2SO_4** will promptly precipitate it. The filtrate contains the alkalies (first group) alone, which are examined as above.

THIRD AND FOURTH GROUPS. Al, Cr, Ni, Co, Fe, Mn, Zn, Ur.

§ 13. To a part of the liquid, from which groups V. and VI. have been removed by **H_2S**, or from which they were originally absent, **NH_4OH** is added to alkaline reaction. A precipitate produced by this, is for the present disregarded, and **$(NH_4)_2S$** is added. If a precipitate is formed by either **NH_4OH** or **$(NH_4)_2S$**, the whole of the liquid is treated in like manner, then gently warmed, filtered, and the precipitate washed with water, to which some ammonium sulphide has been added, to prevent the oxidation of the sulphides in contact with air. In presence of

Ni the filtrate usually contains some **NiS** in solution, which renders it dark brown and turbid.

§ 14. The filtrate and washings are united, and tested for the groups I. and II. as previously directed. As the excess of $(NH_4)_2S$ interferes with these reactions, it is best to evaporate the filtrate to one-half of its volume: **HCl** is then added, and the liquid boiled to destroy any ammonium hyposulphite, which may have formed. After this the detection of the bases of groups I and II is conducted according to § 6.

§ 15. The well washed precipitate of groups III and IV (§ 13) is transferred from the filter to a small flask and digested at a gentle heat with dilute **HCl** (1 : 5). If a residue remain, it is separated by filtration and filtrate and residue examined.

The filtrate may contain **Fe, Mn, Zn, Al, Cr, Ur,** and some of the salts of the alkaline earths. Its examination is conducted according to § 17.

The residue may be white from precipitated **S**, or black and may then contain **NiS, CoS**, and in exceptional cases a little **FeS**, left undissolved. It is treated as follows:

§ 16. A small portion is tested in the oxidation flame with microcosmic salt. A blue bead indicates **Co** and would not permit the recognition of **Ni**; a bead red while hot, yellow when cold, indicates **Ni** and absence of **Co**.*

If **Co** is present, the color of the blue bead will not be interfered with by the presence of **Ni** and therefore **Co** must be removed before **Ni** can be detected. In that case the residue of the sulphides is dissolved in hot concentrated nitric, or nitromuriatic acid, the solution is concentrated by evaporation and neutralized by Na_2CO_3. Either of the following methods may now be adopted.

a. An excess of potassium nitrite is now added and a few drops of acetic acid. The yellow precipitate of potassio-cobaltic nitrite (example XXIII., 6.) is not filtered off till after 24 hours; the filtrate, after being again tested for any residue of **Co** by another addition of KNO_2, is finally treated with **NaOH**, which precipitates green $Ni(OH)_2$.

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* Small quantities of Co may be recognized in the wet way. The mixture of NiS and CoS is dissolved in hot concentrated HNO_3, precipitated by KOH and the precipitate separated by filtration. Without washing the precipitate is transferred to a testtube, solid KOH is added and a little water and the mixture is boiled. Blue color of the solution indicates Co.

b. A more expeditious way to separate **Ni** consists in adding to the neutralized solution **KCN** until the precipitate, formed at first, has redissolved. **Bromine** water is now added until the liquid remains yellow after shaking, and it is then boiled. A black precipitate of Ni_2O_3 will contain the **Ni** present, while **Co** remains in solution as potassium cobalti-cyanide. (Instead of bromine, chlorine water or a solution of sodium hypochlorite, **NaClO,** may be added until the odor remains after shaking.)

§ 17. The filtrate (§ 15) containing the rest of the metals of groups III. and IV. is boiled to remove H_2S and, if **Fe** is present, this must be oxidized by boiling with some $KClO_3$ or HNO_3. The farther method of examination depends upon the presence or absence of **Cr.** This is recognized during the preliminary examination by the green bead it forms with microcosmic salt, or by the color of the **HCl** solution, which, if **Cr** is present, is violet or green.

A. CHROMIUM IS ABSENT.

§ 18. *a. The precipitate by* $(NH_4)_2S$ *was of pale color.*

This shows absence of **iron,** presence of **Al, Mn, Zn** (and alkaline earth salts). The filtrate (§ 15.) containing the substances dissolved in **NaOH;** a **precipitate** consists of $Mn(OH_2)$. This is tested on platinum foil with Na_2CO_3 and KNO_3 according to example XIX. 7. The filtrate from this precipitate is divided into two portions. One of them is acidulated with **HCl** and then supersaturated with NH_4OH; a precipitate indicates **Al,** (verify with $Co(NO_3)_2$ before the blow-pipe). The other portion is treated with H_2S; a precipitate indicates **Zn,** to be confirmed with $Co(NO_3)_2$ before the blowpipe.

§ 19. *b. The precipitate by* $(NH_4)_2S$ *was of dark color.*

This indicates the presence of **iron** and may contain **Ur, Al,** etc. besides, as their paler color is hidden by the dark iron sulphide. The hydrochloric acid solution, § 15, is saturated by Na_2CO_3 until a precipitate forms, which does no longer disappear by shaking and which is redissolved in a little acetic acid. Sodium acetate, $NaC_2H_3O_2$, is added and the liquid boiled, until the precipitate is covered by a colorless liquid. Should this be of brown or yellow color, more acetate of sodium must be added or boiling continued longer. (Compare example XVIII. 18.) The precipitate contains **Fe** and **Al,** the filtrate **Mn** and **Zn.**

§ 20. The precipitate of **Fe** and **Al**, after washing, is dissolved in a little **HCl**, then excess of pure **NaOH** is added and the liquid boiled. The precipitate consists of **$Fe_2(OH)_6$** which is confirmed by dissolving in **HCl** and testing with potassium ferro-cyanide or sulphocyanide. (See ex. XVIII. 15 and ff.)

The filtrate from **$Fe_2(OH)_6$** is acidulated with **HCl** and then **NH_4OH** added to alkaline reaction. Precipitate consists of **$Al_2(OH)_6$**. A deception may here occur from precipitation of silica or alumina already present in the **NaOH**, if this is not absolutely pure. In such case **$Ba(OH)_2$** may be employed intead of **NaOH**.

§ 21. Into the filtrate (§ 19) containing **Zn** and **Mn** a current of **H_2S** gas is passed: **Zinc** precipitates as **ZnS**. This is separated by filtration, the filtrate again treated with **H_2S** to insure that all the Zinc is removed, and, when no more precipitate is formed, **NH_4OH** and afterwards **$(NH_4)_2S$** is added. A flesh colored precipitate contains the manganese as **MnS,H_2O**. (See ex. XIX. 4.)

B. CHROMIUM IS PRESENT.

§. 22. If chromium is present as a salt of **Cr_2O_3**, the solution will have a green or violet color, if as **CrO_3**, its color will be yellow or red.

§. 23. The **HCl** solution which has been treated with **$KClO_3$** or **HNO_3** (§ 17.), at boiling heat, is carefully neutralized with **Na_2CO_3**, without forming a permanent precipitate. To the liquid, which must be quite **cold**, **$BaCO_3$**, suspended in water, is added, **without applying heat**. The mixture is repeatedly shaken up, left standing in a cool place for some time, and, as soon as the supernatant liquid has become colorless, is filtered. In the precipitate **Al**, **Fe**, and **Cr** are to be found, to be treated according to § 24. The filtrate contains **Mn**, **Zn**, to be treated according to § 28.

§. 24. The well washed precipitate must be dissolved in **HCl** and without filtering the **Ba**, which has been dissolved, is precipitated by **H_2SO_4**. After boiling the liquid is filtered, and from the hot solution **NH_4OH** precipitates **Fe**, **Cr** and **Al** as hydroxides. These are filtered off, washed, transferred into a porcelain dish and dissolved in a little concentrated nitric acid. To the solution add some crystals of **$KClO_3$**, boil for some minutes, (if necessary add some more potassium chlorate,) until the liquid has assumed a pure orange color. After addition of an excess of **$NaOH$**, boil again. **Fe** will be precipitated, **Cr** and **Al** remain in solution.

§. 25. Filter and test the precipitate of iron as before, § 20. In case **uranium** is present, this will, in all the above processes of separation, accompany the **iron** and is precipitated as **uranyl hydrate, $UrO(OH)_4$**, together with **$Fe_2(OH)_6$**. To separate **Ur** from **Fe**, the mixture is dissolved in **HCl**, exactly neutralized by **NH_4OH** and precipitated with a mixture of **$(NH_4)_2S$** and **$(NH_4)_2CO_3$**. Only **FeS** is thereby precipitated, while **Ur** (together with the rarer earths) remains in solution. The iron is filtered off, the filtrate acidulated with **HCl**, boiled, oxidized with **HNO_3** and finally precipitated by **NH_4OH**. Yellow **$UrO(OH)_4$** falls. Confirm by microcosmic bead (yellow while hot, greenish when cold), also by solution in **HCl**, and addition of potassium ferrocyanide when a red brown precipitate of uranium ferrocyanide is produced.

§. 26. The alkaline filtrate from **$Fe_2(OH)_6$** is acidulated by **NH_4OH**. The precipitate consists of **$Al_2(OH)_6$**. Confirm with cobalt solution before the blowpipe.

§. 27. **Cr.** The alkaline filtrate removed from **$Al_2(OH)_6$** is colored yellow by the presence of **chromic acid**. It is acidulated with a little acetic acid and **$Pb(C_2H_3O_2)_2$** is added, which precipitates yellow lead chromate, **$PbCrO_4$**.

§. 28. **Mn** and **Zn.** The filtrate (§23) from the precipitate by **$BaCO_3$** is freed from baryta by **H_2SO_4**, filtered, boiled and from the boiling solution **Mn** and **Zn** are precipitated by **Na_2CO_3**. A small portion of the precipitate is tested for **Mn** by **KNO_3** and **Na_2CO_3** (example XIX.). In case **Mn** is found present, the rest of the precipitate is dissolved in acetic acid and treated with **H_2S**. This precipitates **Zn** as white **ZnS**. In the filtrate **Mn** is precipitated by **NH_4OH** and **$(NH_4)_2S$**. (§ 21.)

§ 29. Distinction between **ferrous** and **ferric** salts. As in the systematic course of qualitative analysis **iron** is always separated as a **ferric** salt, it becomes necessary to resort to the **original substance**, when it is to be determined whether **Fe** is present in the **ferrous** or the **ferric** state. To detect a **ferrous** compound, **red potassium ferri-cyanide, $K_6Fe'''(CN)_{12}$**, is added to the acidulated solution of the substance. It produces with **ferrous** salt a blue precipitate: **Turnbulls blue,** $Fe''_3(CN)_6.Fe'''_2(CN)_6$; **ferric** salts are detected according to example XVIII, 11. etc. These reactions can only succeed, however, when other substances are absent, with which the reagents employed produce colored precipitates, for red prussiate of potash produces such with most metals. On the other hand it must be noted that dissolving the substance in nitric acid, or even in hydrochloric acid when peroxides, chromates, nitrates, etc., are present, the ferrous compounds, originally present, are converted into ferric.

§ 30. Should it become desirable, for any reason, to separate the metals of groups III and IV by means of barium carbonate, even though chromium be absent, then the filtrate (§ 23.) containing **Mn** and **Zn** is treated according to § 28; while the precipitate produced by $BaCO_3$ is treated according to § 24 and following, to separate **Fe** and **Al**.

C. PHOSPHATES AND OXALATES OF ALKALINE EARTHS ARE PRESENT.

§ 31. **Oxalates.** A portion of the precipitates by $(NH_4)_2S$ is boiled for some time with an excess of Na_2CO_3 and filtered, while hot: the filtrate is acidulated with **acetic acid** and then treated with $CaCl_2$. A precipitate indicates CaC_2O_4. Confirm according to example XXXVI.

§ 32. When according to the preceding test **oxalic acid** has been found **present,** the rest of the $(NH_4)_2S$ precipitate must be dried and ignited in a porcelain crucible to decompose the oxalic acid. The residue is then dissolved in hydrochloric acid, supersaturated with NH_4OH and precipitated by $(NH_4)_2S$. The alkaline earths, whose oxalates had before been precipitated, will now remain in solution and are to be detected in the filtrate according to § 6.

If the reactions in § 31 have proven the **absence** of **oxalic acid,** the rest of the precipitate is treated at once as follows.

§ 33. The precipitate by $(NH_4)_2S$ (either originally free from oxalic acid, or freed from it according to § 32) is digested with **HCl** according to § 15. A black residue indicates **Ni** and **Co** and requires treating according to § 16. The solution is oxidized with either HNO_3 or $KClO_3$ (to convert **Fe** into **ferric** salt) and in small portions of it **iron** and **phosphoric** acid are sought after as follows:

§ 34. **Iron** is detected by **$KCNS$** or by **$K_4Fe\ (CN)_6$**.

§ 35. **Phosphoric acid.** A small portion of the solution § 33 in **HCl** is boiled to remove **H_2S** and added drop by drop to avoid excess, to a solution of **ammonium molybdate** in nitric acid. A yellow precipitate indicates **H_3PO_4**. (Compare also the distinctive reactions of phosphoric and arsenic acid further on, C. Detection of acids § 66.) Or if the examination § 34 has prove **Fe absent,** a little excess of sodium acetate may be added to the **HCl** solution, § 33, (which must not be too acid) and then a single drop of **Fe_2Cl_6**. Phosphoric acid is precipitated as yellowish white, flocculent **ferric phosphate, $Fe_2(PO_4)_2$.**

§ 36. The rest of the **HCl** solution of the precipitate by **$(NH_4)_2S$** (§ 33) is carefully neutralized by **Na_2CO_3**, (if a precipitate falls, it must be re-dissolved by a little acetic acid) and sodium acetate is added. If in absence of iron this does not color the solution red (by the formation of ferric acetate) ferric chloride must be added until the red color appears. The liquid is now heated until the precipitate separates and the supernatant liquid becomes colorless. The precipitate contains **Fe, Al,** and **H_3PO_4;** the filtrate: **Mn, Zn** and the alkaline earths freed from phosphoric acid.

§ 37. **Alumina.** The precipitate, containing **Fe, Al** and **H_3PO_4,** is filtered off, washed and then boiled with an excess of **$NaOH$**. The alkaline filtrate contains the alumina, to be precipitated by **HCl** and **NH_4OH**. (§ 20.)

§ 38. **Phosphoric acid**. The residue of the precipitate, § 37, after boiling with **$NaOH$,** is dissolved in **HCl,** neutralized with **NH_4OH** and **$(NH_4)_2S$** added in excess. The filtrate containing the phosphoric acid is precipitated by addition of **NH_4Cl, NH_4OH** and **$MgSO_4$**.

§ 39. **Mn, Zn, Ba, Sr, Ca, Mg**. To the filtrate from the precipitate produced by **Fe_2Cl_6** and **$NaC_2H_3O_2$**, (§ 36.) **NH_4OH, NH_4Cl** and **$(NH_4)_2S$** are added. A precipitate contains **ZnS** and **MnS**. A portionof this is tested for **Mn** according to § 28, the rest is dissolved in **HCl, H_2S** is expelled by boiling, and the solution examined for alkaline earths according to § 6.

§ 40. **Simultaneous presence of chromium and phosphoric acid** gives rise to special difficulties. The separation of phosphoric acid from the alkaline earths, according to the method described in § 56, can be effected only if chromium is absent. For solutions of chromium salts are not precipitated by boiling with sodium acetate, and interfere considerably with the precipitation of **Al** and **Fe**. In this case the bases are separated by $BaCO_3$ (the presence or absence of **Ba** being first ascertained in the original solution). The presence of **Fe** and of phosphoric acid in the HCl solution of the precipitate by $(NH_4)_2S$ having been ascertained according to § 34 and 35, another part of the solution is treated with $(NH_4)_2SO_4$. The precipitate of $BaSO_4$ and $SrSO_4$ is boiled with a mixture of K_2CO_3 and K_2SO_4, (see example XL. 6) which converts **Sr** into $SrCO_3$ and leaves $BaSO_4$ unaffected. To the rest of HCl solution enough Fe_2Cl_6 is added (if iron is not present in sufficient quantity) that NH_4OH may produce a yellow precipitate with a drop of the solution. The liquid is evaporated nearly to dryness, the residue dissolved in water, most free acid carefully neutralized with Na_2CO_3 and an excess of $BaCO_3$ added, the mixture shaken and left standing in a cool place. The precipitate produced by the barium carbonate is dissolved in HCl, **Ba** removed by H_2SO_4 and then NH_4OH added. This precipitates **Al**, **Cr**, **Fe** and **phosphoric acid**, which are treated according to § 57. The filtrate is then freed from **Ba** by addition of H_2SO_4 and treated according to § 39.

FIFTH AND SIXTH GROUPS.

Hg, Ag, Pb, Bi, Cu, Cd; As, Sb, Sn, (Au).

§ 41. If the original substance is in aqueous solution, it is acidulated by a little HCl. If the solution is an acid, some water must be added for dilution. Any precipitate occasioned by these additions is disregarded for the present, * and H_2S is added.

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* From an **acid** solution H_2O precipitates basic salts of **Bi** and **Sb**.

From **aqueous** (or acid) solution HCl precipitates $AgCl$, Hg_2Cl_2 and $PbCl_2$.

From **alkaline** solution HCl may precipitate $AgCl$, $PbCl_2$, As_2S_3, SnS_2, etc., (for instance PbO in solution of $NaOH$, ammonical solutions of $AgCl$, As_2S_3, etc.

From an aqueous solution of **Schlippe's salt**, Na_3SbS_4, hydrochloric acid precipitates Sb_2S_5, while H_2S gas escapes.

From solutions of some **double cyanides** HCl precipitates insoluble cyanides with evolution of **hydrocyanic acid**, HCN.

Such precipitates may be examined separately, but as H_2S converts them into sulphides, it is unnecessary to filter them off, for they are found among the other sulphides of the V and VI groups.

HCl also precipitates **silica** from silicates in alkaline solution. Their special examination is described further on, § 93.

Cyanogen compounds are also examined by special methods, § 98.

If this produces a precipitate, the liquid must be warmed and **H_2S** gas passed until the substances capable of being precipitated by it are removed from the solution. The completion of the operation is known by the liquid after thorough shaking, still retaining the odor of **H_2S**, and by testing a portion of the filtrate, which must not yield any more precipitate on the further addition of **H_2S**. It is very important to insure the completeness of this precipitation, as portions left behind would interfere with further examination.

If the solution of the original substance contained **too much free nitric acid**, only a flocculent, yellowish precipitate of **S** is precipitated by the introduction of **H_2S**, while nitrous vapors escape. In such case the free acid must be removed by evaporation, and then water added to the liquid.

The sulphides of groups V and VI are all colored. If **H_2S** produces a white precipitate, or even a milky turbidity of precipitated sulphur, it indicates the absence of the metals of the V and VI groups and the presence of a ferric salt, or a chromate. In the latter case the red or yellow solution is changed into a violet or green one.

The precipitated sulphur needs no attention, the liquid, without filtering, is rendered alkaline by **NH_4OH**, and then tested by **$(NH_4)_2S$** for the metals of the III and IV groups.

§ 42. The precipitate by **H_2S**, containing the sulphides of the metals of groups V and VI is separated by filtration. The filtrate is tested as directed in § 13., for the metals of the III and IV. groups. The precipitate, after thorough washing with water, is transferred to a small glass flask, by perforating the filter with a glass rod and washing the precipitate down by means of the spritz flask. After the precipitate has subsided, the wash-water is decanted and **yellow ammonium sulphide, $(NH_4)_2S_2$,** is added and some time allowed for thorough digestion. This operation serves to separate the metals of the VI group, which dissolve, from those of the V group, which remain as insoluble residue. The solution is separated from the residue by filtration. The residue is examined according to § 43. The filtrate is treated with excess of **HCl**. If this occasions a colored precipitate, it indicates the presence of metals of group VI, whose examination is described in § 48. If the precipitate is white, it contains only sulphur, and the metals of group VI are absent.

FIFTH GROUP: Hg, Ag, Pb, Bi, Cu. Cd.

§ 43. The part of the precipitate by $\mathbf{H_2S}$, which did not dissolve in $(NH_4)_2S_2$ is washed with $(NH_4)_2S_2$ diluted with water and afterwards with $\mathbf{H_2O}$, and then transferred to a glass flask and boiled with dilute $\mathbf{HNO_3}$, (of specific gravity 1,2). The black residue consists of **HgS**, § 44; the filtrate is examined according to § 45.

§ 44. **Mercury.** If the residue insoluble in $\mathbf{HNO_3}$ is heavy and **black**, **HgS** is indicated; if **white** or **yellow**, it contains sulphur derived from the oxidation of the sulphides. Errors may arise from the following causes. If **mercurous** salts are present and the $\mathbf{H_2S}$ precipitate is not treated sufficiently with the yellow ammonium sulphide, $\mathbf{Hg_2S}$ remains, instead of **HgS**. The mercurous sulphide, on boiling with $\mathbf{HNO_3}$ is partly dissolved, partly converted into **white** or **gray** $\mathbf{Hg(NO_3)_2.HgS}$, which remains undissolved. In this case **Hg** may be detected in the residue, by igniting it on charcoal with dry sodium carbonate. (See example XXIX.) Another error may arise, even when **mercuric** salts are present, by imperfect precipitation by $\mathbf{H_2S}$ and subsequent use of $\mathbf{(NH_4)_2S}$. A white residue, insoluble in $\mathbf{HNO_3}$ will then remain as before.

To prove the presence of **Hg** in the black residue, **HgS**, a portion of it is dried, mixed with dry $\mathbf{Na_2CO_3}$, and heated in a glass-tube.

Another portion is boiled with nitro-muriatic acid until it dissolves perfectly, only leaving a white or yellow residue of **S**. The solution is diluted with water, filtered and neutralized with $\mathbf{Na_2CO_3}$, until a precipitate begins to form: this is redissolved by a drop of **HCl** and **KI** added, which produces a red precipitate of mercuric iodide.

Another portion may be treated with concentrated **HCl** and some $\mathbf{KClO_3}$ to convert **HgS** into $\mathbf{HgCl_2}$. Cautious addition of stannous chloride will precipitate first $\mathbf{Hg_2Cl_2}$, and then **Hg**.

To ascertain whether **mercurous** or **mercuric** salt is present, **HCl** is added to the original substance, when a **mercurous** salt will be indicated by a white precipitate of $\mathbf{Hg_2Cl_2}$, turning black on addition of $\mathbf{NH_4OH}$. (See example, I., 4.) In the filtrate from the white precipitate of calomel, **mercuric** salt is shown by **$SnCl_2$** or **KI**.

It must be remembered that when oxidizing agents are present in the original substance or used for solution (such as **HNO_3**, chromates, peroxides, etc.), the mercurous compounds of the original substance are converted into mercuric.

§ 45. **Lead** and **Silver.** The filtrate (§ 43) from **HgS**, insoluble in **HNO_3**, contains the rest of the metals of group V. To it some dilute **H_2SO_4** is added. If this produces a precipitate of **$PbSO_4$**, more **H_2SO_4** is added, to insure more complete conversion of the lead, and the solution is evaporated in the water-bath until all the **HNO_3** is expelled. The residue is diluted with water containing some **H_2SO_4** and filtered. A part of the precipitate of **$PbSO_4$** is tested before the blowpipe with **Na_2CO_3**, when a ductile metallic globule of **Pb** is produced surrounded with a coating of **PbO.** Another part is dissolved in ammoniacal solution of tartaric acid, from which it is precipitated by **$K_2Cr_2O_7$**.

The filtrate from **$PbSO_4$** is treated with **HCl** which precipitates silver as **AgCl.** This precipitate, well washed must dissolve completely in **NH_4OH**, and be reprecipitated from this solution by **HNO_3**.

§ 46. **Bismuth.** The filtrate from **AgCl** is supersaturated with **NH_4OH**. A white precipitate consists of **$Bi(OH)_3$**. The precipitate is filtered off, washed and dissolved in **very little HCl**; the solution is poured into water. A white precipitate consists consists of **BiOCl.** Confirm before blowpipe according to example XXVI., 3.

§ 47. **Copper** and **Cadmium.** If **Cu** is present, the ammoniacal filtrate from bismuth hydrate is **blue.** To separate **Cd** from **Cu**, the solution containing both metals is precipitated by **H_2S**, the precipitate is well washed and boiled with **H_2SO_4** diluted with water 1:5. This leaves **CuS** as residue, while the solution contains **Cd**; this solution is again diluted and **CdS**, precipitated by **H_2S**.

Another method of separation consists in adding **KCN** to the ammoniacal solution mentioned above until the precipitate, formed at first, is redissolved and the solution becomes colorless. Now **H_2S** is added, which precipitates **CdS** alone, but leaves the **Cu** in solution. (Compare examples XXVII., 10, and

XXVIII. 7.) If **Cu** be absent, **Cd** is detected at once by **$(NH_4)_2S$**.

SIXTH GROUP. As, Sb, Sn, (Au).

§ 48. To the solution of the metals of the sixth group in **$(NH_4)_2S$**, (or if **Cu** be present, in **Na_2S** or **K_2S**) obtained in § 42, **HCl** is added to acid reaction. If no metals of the VI group are present, the addition of **HCl** will produce only a white, milky precipitate of sulphur, derived from the yellow ammonium sulphide. If the metals are present the precipitate is colored. It is gently heated to favor coherence, filtered off and washed.

The mixture of the sulphides is gradually heated with **concentrated HCl.** A yellow residue contains **As,** the filtrate **Sn** and **Sb.** A dark residue (if **Cu** has been excluded) indicates **Au** or **Pt.**

§ 49. **Arsenic.** The yellow arsenic pentasulphide, As_2S_5* is dissolved in concentrated **HCl,** to which some **$KClO_3$** has been added: the solution is supersaturated with **NH_4OH** and **NH_4Cl** and **$MgSO_4$** added. The white precipitate consists of magnesium arsenate, **$Mg(NH_4)AsO_4$.** To confirm, the precipitate is filtered off, washed, and a portion tested with **$AgNO_3$.** The color changes from white to brown-red from the formation of silver arsenate, **Ag_3AsO_4.**

§ 50. Another portion of the precipitated **magnesium arsenate,** or of the **arsenic pentasulphide** † obtained in § 49, after washing and drying is mixed with a sixfold weight of a mixture of dry potassium cyanide and sodium carbonate. It is transferred to a narrow glass tube, closed at the end, and carefully heated. Any water, which may condense at first, is removed by a strip of filter paper and then higher heat applied. The arsenic is reduced and sublimes, forming a mirror in the cooler part of the tube. If the closed end be now cut off and the tube heated in a somewhat inclined position, garlic odor will be perceived and the **As** mirror will be gradually oxidized to **As_2O_3**, which deposits itself at the upper cooler end of the tube.

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* **As_2S_3**, by treating with yellow ammonium sulphide, and then with **HCl**, is converted into **As_2S_5**. $As_2S_3 + 2[(NH_4)_2S_2] + (NH_4)_2S = 2[(NH_4)_3AsS_4]$. $2[(NH_4)_3AsS_4] + 6HCl = As_2S_5 + 3H_2S + 6NH_4Cl$.

† When **As_2S_5** is heated with **KCN** and **Na_2CO_3**, not all of the arsenic is obtained in the **free** state, on account of the formation of potassium sulpharsenate, **K_3AsS_4**, which is not affected by **KCN**. When free **S** is present, in addition, as will always be the case after employment of yellow ammonium sulphide, §48, there will be still less **As** liberated. To avoid this source of error the mixed precipitate of **As_2S_5** and **S** is treated with **NH_4OH**, which dissolves the arsenic sulphide, and leaves sulphur undissolved. The ammoniacal solution is evaporated to dryness and the residue ignited with **KCN** and **Na_2CO_3** as directed.

§ 51. Only the alkali salts of **arsenous** and **arsenic acid** are soluble in water, all others only in acids. The distinctive reactions between the two acids are:

a. The mixture of **NH_4OH, NH_4Cl,** and **$MgSO_4$** precipitates only **arsenates.**

b. Silver nitrate precipitates from **arsenites, yellow** silver arsenite, soluble in **NH_4OH**, which, on boiling, deposits metallic silver; from **arsenates, brown-red** silver arsenate is precipitated, also soluble in ammonia, but depositing no silver on boiling. (Compare example XXXIII. 10).

c. A solution of **As_2O_3** in excess of **NaOH** gives, on addition of a little **$CuSO_4$**, a blue solution. On boiling this the **cupric** salt is reduced to **cuprous,** while the arsenite is oxidized to **arsenate** of sodium. Hence a red precipitate of **Cu_2O** will fall only when arsenites, not when arsenates are present.

$$As_2O_3 + 14NaOH + 4CuSO_4 = 2Cu_2O + 2Na_3AsO_4 + 4Na_2SO_4 + 7H_2O.$$

§ 52. **Tin** and **Antimony.** The solution in concentrated **HCl** (obtained § 48) is diluted with water and, if too acid, nearly, but not quite, neutralized with **NaOH**. A strip of **pure zinc** (free from lead or arsenic) is placed into the solution. (A few drops of this may be tested on platinum foil, the zinc is held into it, and if **Sb** is present, a black spot of reduced antimony will adhere to the platinum, see example XXXI.) When the reduction is ended, the surplus of zinc is removed, the solution of **$ZnCl_2$** poured off, the reduced metals washed by decanting, and **HCl** added to the residue of **Sn** and **Sb.** This dissolves **Sn** and leaves **Sb.** The solution of **$SnCl_2$** is filtered off from the residue and the presence of **tin** proven by the reduction of corrosive sublimate, (example XXIX. 11. or XXXI. 8. or by precipitating brown stannous sulphide, **SnS,** by **H_2S,** or purple of Cassius by gold chloride (XXXI. 16.)

The residue of **Sb** is dissolved in a little aqua regia and poured into water, when **SbOCl** will be thrown down, soluble in tartaric acid, and precipitable from this solution by **H_2S** as orange **Sb_2S_3** (XXXII. 5.)

§ 53. The different **degrees of oxidation of tin and antimony** may be determined as follows: A **stannous** solution is recognized by its reducing action on $HgCl_2$. A **stannic** solution, feebly acidulated, when added to a boiling, saturated solution of Na_2SO_4 produces a white precipitate.

A solution of **antimonic** salt, boiled with HCl and KI, liberates iodine. $Sb_2O_5 + 4KI + 10HCl = 4I + 4KCl + 2SbCl_3 + 5H_2O$.

In a solution of Sb_2O_3 in $NaOH$ there is produced by $AgNO_3$ a black precipitate of a mixture of Ag_4O and Ag_2O. The addition of NH_4OH dissolves the argentic oxide and leaves the deep-black argentous oxide as residue. $Sb_2O_3 + 8AgNO_3 + 8NaOH = 2Ag_4O + Sb_2O_5 + 8NaNO_3 + 4H_2O$.

§ 54. **Gold.** If heating of the sulphides, according to § 48, with HCl leaves a brown residue, or if the yellow color of the arsenic sulphide is darker than it should be, **gold** (and **Pt**) may be present, provided care has been taken to exclude copper by using **potassium** or **sodium** instead of **ammonium sulphide** in digesting the mixed sulphides of the V and VI groups. In this case reduction of the original solution by oxalic acid, ferrous sulphate, or sulphurous acid, will precipitate the gold; the precipitate is collected, dissolved in aqua regia, and confirmatory tests made according to example XLII.

SECOND METHOD FOR SEPARATING As, Sn and Sb.

§ 55. The mixture of the sulphides of group VI (§48) is heated with concentrated HCl to which some $KClO_3$ has been added, gently at first, then to a higher temperature, until at last only a little sulphur remains undissolved. The solution is filtered and supersaturated with concentrated solution of $NaOH$ and then one-fifth of its volume of alcohol is added. **Sodium metantimonate,** $NaSbO_3$, is precipitated, to be tested before the blowpipe with Na_2CO_3 on charcoal, or by dissolving in HCl and reducing by Zn upon platinum foil.

The filtrate is boiled, to remove alcohol, then acidulated with tartaric acid, to prevent the precipitation of tin, and lastly supersaturated with NH_4OH. The addition of NH_4Cl and $MgSO_4$ will now precipitate arsenic as magnesium ammonium arsenate $Mg(NH_4)AsO_4$, which may be farther tested as above, § 49. The filtrate from this arsenic precipitate contains Sn. It is acidulated with **HCl**, and **H_2S** added, which precipitates stannic sulphide **SnS_2**. This is tested by roasting on charcoal, before the blowpipe in the oxidation flame, and afterward reducing the **SnO_2** thus formed to metallic tin by melting with **Na_2CO_3**.

THIRD METHOD FOR SEPARATING As, Sn and Sb.*

§ 56. The mixture of the sulphides of group VI (§48) is dissolved in concentrated **HCl**, to which some **$KClO_3$** has been added, the free chlorine is expelled by evaporation and the solution brought into a flask or tubulated retort of about 500 cubic centimeters capacity. About 10 to 20 cubic centimeters of solution of ferrous chloride are added, (prepared by dissolving iron, in excess, in hydrochloric acid of specific gravity 1.12) after this hydrochloric acid of specific gravity 1.10 is poured in until the volume of the whole liquid reaches about 150 C.C. A receiver being adapted, the liquid is distilled off until 30 to 35 C.C. remain in the retort. The arsenic is converted into volatile **$AsCl_3$** and distils over, while **Sn** and **Sb** remain in the residue.

$$H_3AsO_4+2Fe''Cl_2+5HCl=AsCl_3+Fe'''_2Cl_6+3H_2O.$$

In the distillate **As** is detected according to example XXXIII. The residue in the retort (or flask) is diluted with water and tin and antimony precipitated by **H_2S**. Their sulphides are then separated either (according to § 52) by dissolving in concentrated **HCl**, reduction by **Zn** and separating the metals by **HCl** or by forming sodium met-antimonate according to § 55.

Detection of small quantities of Arsenic by means of arsenetted hydrogen. (Marsh's method.)

§ 57. To a widemouthed flask, holding about 250 C. C. (half a pint) fit a cork with a double perforation, through one of which passes a funnel tube to near the bottom of the flask, through the other a glass tube (made of hard glass) about 4 Mm thick, bent twice at right angles into a bayonet shape. The second tube passes only a little distance through the cork and is cut off obliquely at the end. The upper portion is drawn out into a jet and projects some distance above the funneltube, see fig. 5.

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* In former editions Bunsens method was given instead of the one now substituted, and as it gives very satisfactory results, it is here repeated in short outline:

§ 56 a. Dissolve the sulphides of group VI in **sodium sulphide**, (made by saturating one-half of a solution of sodium hydrate with **H_2S**, and, after full saturation, adding the other half); add **H_2SO_3** in excess, heat slowly until a boiling heat is reached and all superfluous sulphurous acid expelled.

Tin and antimony are precipitated as sulphides, while arsenic remains in solution as sodium arsenite. Filter and separate **Sn** and **Sb** as above stated, while **As** is precipitated from the filtrate by **H_2S**.

Into the flask some pieces of **pure zinc** are placed and distilled water and **pure sulphuric acid** added through the funnel-tube. A copious evolution of hydrogen will ensue and when sufficient time has elapsed to have all the air expelled from the flask, the gas is ignited at the jet, and burns with a non-luminous flame, which after some time assumes the color of the alkali contained in the glass. **A cold** piece of **porcelain** is now held into the flame, when water will condense upon it, but no stain will be observable if the zinc and acid employed are pure. The flame may be blown out and a piece of paper, moistened with **silver nitrate** solution held into the escaping gas, which must not be blackened. Every thing being thus prepared, the flame is rekindled, and then a little of the liquid to be tested for arsenic is poured into the funneltube. If **As** is present even in very small quantity, the flame will change its color to a blueish-white: a cold piece of porcelain is held into the flame, close to the orifice of the jet as before. A shining brown stain of metallic arsenic will form, which will dissolve quickly in alkaline solution of **sodium hypochlorite.** If antimony is used instead of arsenic, the stain will be of a dark velvety black, and will not dissolve in sodium hypochlorite.

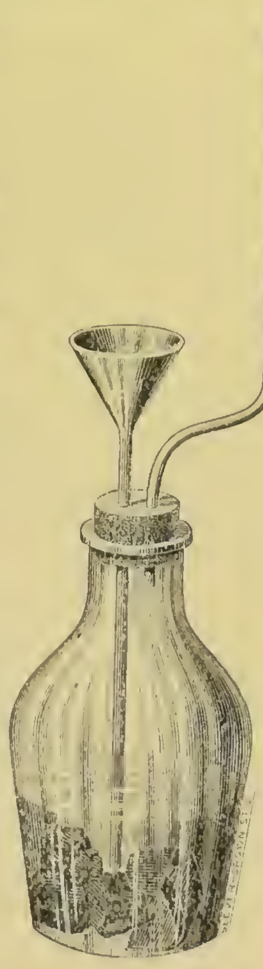
Fig. 5.

If the quantity of arsenic be too small to give a stain on porcelain, paper moistened with silver nitrate solution, held into the cold gas will show a black stain and detect infinitesimal quantities; but antimonetted hydrogen or sulphuretted hydrogen will also stain the paper.

A simpler apparatus may be employed for testing the gas without flame. A testtube is provided with a well-fitting cork, through which a short glass jet is passed. Aluminium foil and solution of caustic soda is placed into the testtube and heated. Hydrogen escapes by the jet and is examined for purity by the silver paper. The liquid to be tested is now added, heat applied and the silver paper will blacken if traces of arsenic are present.

The apparatus figured (fig. 5.) may be modified by substituting for the upright tube a longer one, bent to occupy a horizontal position, and again bent down at the end, so as to dip into a vial with silver solution. If a portion of the horizontal tube be then heated to redness, the arsenetted hydrogen is decomposed and a mirror of arsenic deposited just beyond the heated portion, while any escaping gas will leave its arsenic in the silver solution, reducing the silver to the metallic state. As the gas is **very poisonous, great caution** must be observed to avoid its inhalation.

Analysis of compounds insoluble in water and acids.

§ 58. To this category belong:

1. **$BaSO_4$, $SrSO_4$, $CaSO_4$, $PbSO_4$.**
2. **$AgCl$, $AgBr$, AgI, $PbCl_2$, $PbBr_2$, PbI_2.**
3. Some oxides having been **highly heated: Cr_2O_3, Fe_2O_3, Al_2O_3, SnO_2,** and minerals, such as **chromic iron ore.**
4. **CaF_2.**
5. **C, S.**
6. **Silicates.**

§ 59. An insoluble **black** substance is to be heated on platinum foil in the oxidation flame of the blowpipe. Treated in this manner **coal** will burn, leaving a white residue (**graphite** cannot be burned unless oxygen gas is used instead of air).

If **sulphur** is present, the odor of **SO_2** reveals it. If a specimen be then heated in the glasstube, the sulphur sublimes and collects in brown drops.

§ 60. Any residue remaining after **C** and **S** have been removed is treated with **$(NH_4)_2S$.** If a black color is produced in a lighter colored substance **Pb** or **Ag** are indicated. In case **Pb** or **Ag** are present, they may also be detected by the blowpipe, which is also relied upon to detect **Sn, Cr, sulphuric acid** and **silica.**

For the examination of **CaF_2** and the analysis of **silicates** directions are given further on.

§ 61. If neither **Pb** nor **Hg** are present, the insoluble substance is melted with about four times its weight of **Na_2CO_3,** before the blast lamp in a platinum crucible, until the melted mass is in quiet fusion, after cooling it is dissolved in water. The acids pass into the solution (**H_2SO_4** is detected by **$BaCl_2$** after acidulating the filtrate.) The residue contains **Ba, Sr,** etc, which, after careful washing, are dissolved in **HCl** and separated in the usual manner.

If chromium is present, **$KClO_3$**, in small portions, is added towards the end of the fusion; or else the substance is melted in a porcelain crucible with a mixture of equal parts of **Na_2CO_3** and **KNO_3** for about 10 minutes, the temperature not being allowed to rise too high. In the aqueous solution of the fused mass, **Cr** is detected by acidulating with acetic acid and precipitating with lead acetate.

Highly heated **alumina** and **ferric oxide** will dissolve by protracted heating with a mixture of equal volumes of concentrated sulphuric acid and water.

Stannic oxide, which had been highly heated, is not changed by melting with **Na_2CO_3.** It must be fused in a porcelain crucible with a sixfold weight of a mixture of equal parts of **Na_2CO_3** and **sulphur.** The fused mass is extracted by water, and **HCl** is added, which precipitates **SnS_2**, to be examined according to § 48 and 52.

§ 62. **Lead and silver are present.**

a. The substance is repeatedly boiled with a concentrated solution of **ammonium acetate** by means of which **$PbSO_4$** and **$PbCl_2$** are extracted. In the filtrate **lead** may be detected by **H_2S** and **Cl** by **$AgNO_3$; H_2SO_4** by **$BaCl_2$**. From the residue **ammonium hydrate** extracts **AgCl** (confirmed by reprecipitation with with **HNO_3**). As **AgBr** and **Ag I** are hardly soluble in **NH_4OH,** the residue is better to be treated with aqueous solution of **KCN,** which dissolves the silver salts, and converts them into double cyanides. From this solution **Ag** is again precipitated by **HNO_3.** To find the acids **AgCl, Ag Br** and **AgI** are fused with Na_2CO_3, in a porcelain crucible, and **Cl, Br** and **I** are determined in the aqueous solution of the fused mass. Or else the silver salts are treated with **Zn** and very dilute H_2SO_4 and examined as directed farther on.

The residue remaining after **Ag** and **Pb** have been removed, is then examined according to § 61, for the other bases.

§ 63. b. The substance insoluble in acids is digested for some hours, in a cool place, with solution of $NaHCO_3$, and frequently shaken up. (Na_2CO_3 would dissolve some **Pb**.) The insoluble residue is then separated by filtration, washed with cold water, and H_2SO_4 and HCl determined in the filtrate as usual. The residue is digested with dilute nitric acid, which dissolves out **Pb, Sr** and **Ca** while $BaSO_4$ $AgCl$, $AgBr$ and AgI remain. The latter residue is fused with Na_2CO_3 in a porcelain crucible, the fused mass treated with water, which dissolves Na_2SO_4, $NaCl$, $NaBr$ and NaI, while $BaCO_3$, and **Ag** remain behind and are separated by HCl.

Another way is to show in the mixture the sulphate of barium by boiling with sodium carbonate. (See example XLI); or else the silver is first extracted by KCN, and then $BaSO_4$ is decomposed by Na_2CO_3.

C. DETECTION OF ACIDS.

§ 64. Before proceeding to the analysis of the acids, it is necessary that the bases contained in the substance are known, and those of them removed, which would interfere with the subsequent reactions. When we have alkaline salts or some others, easily soluble in water, no further preparation is generally necessary, than the removal (if present) of members of the **arsenic group** (group VI). In most cases, when the substance does not readily dissolve in water, it is desirable to transfer the acid to sodium, which forms with nearly all the acids salts soluble in water. This is accomplished by boiling the solid substance with an excess of Na_2CO_3, and filtering. With the exception of the earthy phosphates and very few other substances this will give us the acids in the filtrate. Members of the **arsenic** group are removed by acidulating with H_2SO_4 and precipitation with H_2S and filtering off the precipitate. **sulphuric acid** and H_2S, which are thus introduced, must be sought for in the original solution, in which also some of the other acids may be readily found, if they have not already been detected during the examination for bases.

§65. The inorganic acids (to which, for convenience's sake a few of the most common organic are joined) may be subdivided into three groups, according to their behavior with **barium chloride** and **silver nitrate**. They cannot, however, be as strictly and systematically separated by group reagents as the metallic bases, and special methods must be resorted to for their detection and separation.

CLASSIFICATION OF ACIDS.

GROUP I.	GROUP II.	GROUP III.
Precipitated by $BaCl_2$ from neutral solution	Not precipitated by $BaCl_2$. Precipitated by $AgNO_3$.	Not precipitated by $BaCl_2$ nor by $AgNO_3$.
H_2SO_4	HCl	HNO_3
H_2SO_3	HBr	$HClO_3$
$H_2S_2O_3$	HI	$HClO_4$
H_3PO_4	HCN	
H_3PO_3	(and its compounds)	
HF	H_2S	
H_2SiF_6	HNO_2	
H_4SiO_4	$HClO$	
H_3BO_3	$HClO_2$	
H_2CO_3	H_3PO_2	
$H_2C_2O_4$		

I. GENERAL PROPERTIES OF ACIDS.

§66. **Solubility in water.**

There are soluble in water:

1. **All salts** of the following acids:

$HClO_3$; HNO_3; HNO_2; H_2SO_4 (excepting $BaSO_4$, $SrSO_4$, $CaSO_4$, and $PbSO_4$); HCl (excepting $AgCl$, Hg_2Cl_2 and $PbCl_2$;) HBr (excepting $AgBr$, $PbBr_2$, and Hg_2Br_2); HI (excepting AgI, PbI_2, Hg_2I_2 and Cu_2I_2); $H.CHO_2$ (formic acid) and $H.C_2H_3O_2$ (acetic acid).

2. Only the **alkaline salts** of the following acids:

H_2CO_3; H_2CrO_4; H_3AsO_3; H_3AsO_4; H_3PO_4 (and other acids of phosphorus); $\mathbf{H_2SO_3}$; $\mathbf{H_4SiO_4}$; $\mathbf{H_3BO_3}$; $\mathbf{H_2C_2O_4}$. All the rest of the salts of these acids (silicates excepted) are soluble in acids.

3. The **sulphides, single** and **double cyanides** of the alkali metals.

$\mathbf{H_2CO_3}$, $\mathbf{H_2S}$, $\mathbf{H_2SO_3}$, $\mathbf{H_3AsO_3}$, $\mathbf{H_3AsO_4}$ and $\mathbf{H_2CrO_4}$ are found during the examination for bases. When **HCl** is added to the respective salts $\mathbf{CO_2}$, $\mathbf{H_2S}$ and $\mathbf{SO_2}$ are evolved as gases and easily recognized. $\mathbf{CO_2}$ by rendering lime water turbid, $\mathbf{H_2S}$ by blackening lead acetate, and $\mathbf{SO_2}$ by blackening a strip of paper moistened with $\mathbf{Hg_2(NO_3)_2}$.

II. SPECIAL REACTIONS.

Examination for H_2SO_4, HCl, HNO_3 and H_3PO_4.

§ 67. **Sulphuric acid.** The **aqueous** solution of the substance is acidulated by **HCl** and $\mathbf{BaCl_2}$ added; to the **acid** solution $\mathbf{BaCl_2}$ is added at once. Should silver or mercury be present, then $\mathbf{HNO_3}$ must be used to acidulate, and $\mathbf{Ba(NO_3)_2}$ instead of $\mathbf{BaCl_2}$. The solutions must not be too concentrated so that $\mathbf{BaCl_2}$ would be precipitated. $\mathbf{BaSO_4}$ forms a white precipitate, insoluble in water and in all acids.

Hydrochloric acid. Aqueous solutions are acidulated with $\mathbf{HNO_3}$ and tested with $\mathbf{AgNO_3}$. The white curdy precipitate is completely soluble in $\mathbf{NH_4OH}$.

Nitric acid. A few drops of recently prepared concentrated solution (or a small crystal) of $\mathbf{FeSO_4}$ are added to some concentrated $\mathbf{H_2SO_4}$, which must be cool. The aqueous solution of the substance is then carefully poured upon it, so as to form a separate layer. A brown ring at the place of contact will indicate $\mathbf{HNO_3}$. (Compare example IV 8.) Another very sensitive reaction for $\mathbf{HNO_3}$ is obtained by adding to about 1 C.C. of the solution a small crystal of **diphenyl-amine**, $\mathbf{NH(C_6H_5)_2}$, and then about an equal volume of concentrated sulphuric acid. If $\mathbf{HNO_3}$ is present the solution becomes **blue.**

§ 68. **Phosphoric acid.** As in the following reactions phosphoric acid cannot be distinguished from arsenic acid, it is necessary to remove **As** by $\mathbf{H_2S}$, before examining for $\mathbf{H_3PO_4}$.

a. A substance **soluble in water** can only contain **alkali salts** of phosphoric acid. Addition of $\mathbf{NH_4Cl}$, $\mathbf{NH_4OH}$ and

$MgSO_4$ to the aqueous, solution precipitates phosphoric acid as **$Mg(NH_4)PO_4$**.

If alkaline carbonates are present they must first be converted into chlorides by **HCl** or else **$MgCO_3$** will be precipitated. The acidulated solution is boiled to expel **CO_2**, then **NH_4Cl** and **NH_4OH** in excess are added and lastly **$MgSO_4$**.

b. An **acid** solution of the substance is neutralized with **NH_4OH** until a precipitate falls; this is redissolved in a little **$HC_2H_3O_2$**, some **$NaC_2H_3O_2$** added and then one drop of **Fe_2Cl_6**. A flocculent, yellowish precipitate of **$Fe_2(PO_4)_2$** falls if phosphoric acid is present.

c. The acid solution of the substance (best in **HNO_3**) is treated according to example VII. 8. with **ammonium molybdate**. The precipitate of ammonium phospho-molybdate is dissolved in **NH_4OH**, then **NH_4Cl** and **$MgSO_4$** are added, which precipitate **$Mg(NH_4)PO_4$**. This is separated by filtration and by the addition of **$AgNO_3$**, is converted into yellow **Ag_3PO_4**.

Examination for other acids.

§ 69. A specimen of the solid substance is placed into a test tube and concentrated **H_2SO_4** added. If no reaction ensues at once, it is heated gently. The following appearances are noted:

1. **Evolution of colorless gas.** **HCl, HNO_3, CO_2, H_2S, SO_2** (either from sulphites or hyposulphites) **HF**, (whose vapors attack the glass) **CO** (from decomposition of cyanides, oxalates, or other organic salts,) acetic acid, formic acid, etc.

2. **Evolution of colored gas.** **Br**, brownish-yellow; **HNO_2** (and other oxides of nitrogen) red-brown; **I**, violet; **Cl** (and its oxides) greenish-yellow.

3. **No gas, nonvolatile acids.** **H_3PO_4, H_4SiO_4, H_3BO_3** (the latter to be easily identified by green flame coloration (see example VIII. 6.

4. **The substance blackens:** Organic acids, leaving a residue of **C**, when **destroyed** by **H_2SO_4**.

§ 70. **Hydriodic** and **hydrobromic acid**. To detect **iodine** the aqueous solution of the substance is acidulated with **H_2SO_4**, and starchpaste, and then a drop of the solution of **KNO_2** is added. A blue color indicates **I**.

Instead of recognizing the color of **I** by starchpaste, **CS_2** or

benzol or **chloroform** may be added and the liquid shaken after the addition of KNO_2. The red color of the chloroform, etc., will indicate **I**.

To detect **bromine** CS_2 or chloroform or either is added to the solution of the substance and then **chlorinewater**, drop by drop. The chloroform etc., will be colored yellow by **Br**, liberated from the solution, if shaken thoroughly after every addition of chlorinewater.

If **I** and **Br** are present simultaneously, **I** is liberated first, then discolored by formation of ICl_3, or HIO_3 and at last **Br** is set free and produces the yellow color. Compare example XXXIX, page 49.

§ 71. **Separation of Cl Br and I.** Iodine and bromine are first determined according to the preceding § 70. To detect chlorine the solution, which must contain **only alkaline bases** (compare § 64.), is mixed with Na_2CO_3 and $K_2Cr_2O_7$, evaporated to dryness, and the residue fused in a porcelain crucible (any remaining **I** or **Br** will then be expelled.) The melted mass is broken into small fragments and introduced into a small glass retort, to which a receiver has been fitted, which is kept cool. Strongly concentrated H_2SO_4 is now poured into the retort and heat applied. By this proceeding **I** and **Br** which still may remain are set free from the iodides and bromides, while **Cl** combines with the chromic acid, to form **chlorochromic acid**, CrO_2Cl_2, which is volatile and passes into the receiver, where it condenses in dark-brown oily drops. To the distillate H_2O is carefully added (or else water is placed into the receiver at first.) and the solution tested for **Cr**, either by heating with alcohol and precipitating by ammonia water, or by saturating with NH_4OH and by adding lead acetate. (Compare example XVII.) If **Cr** is found in the distillate, it proves that **Cl** has been present, for by these means only has **Cr** been converted into a volatile compound. The reactions occur according to the following equations:

1.) $6KI$ (or KBr) $+K_2Cr_2O_7+7H_2SO_4=6I$ (or Br) $+3K_2SO_4+K_2SO_4.Cr_2(SO_4)_3+3H_2O$.

2.) $4NaCl+K_2Cr_2O_7+3H_2SO_4=2CrO_2Cl_2+K_2SO_4+2Na_2SO_4+3H_2O$.

3.) $CrO_2Cl_2+4NH_4OH=(NH_4)_2CrO_4+2NH_4Cl+2H_2O$.

§ 72. **AgCl, AgBr, and AgI.** Silver bromide is yellowish, very little soluble in NH_4OH, or in $(NH_4)_2CO_3$; silver iodide is yellow and almost absolutely insoluble in NH_4OH or in $(NH_4)_2CO_3$; while silver chloride is white and very soluble in ammonium hydrate or carbonate. If therefore a silver precipitate containing the three mixed salts is treated with ammonium hydrate (or still better with neutral carbonate) all the **AgCl** and a little **AgBr** are dissolved, while **AgI** is left in the residue, and becomes whitish-yellow from absorption of ammonia. HNO_3 reprecipitates **AgCl** and **AgBr** from the ammoniacal solution.

To detect **AgCl, AgBr** and **AgI** when all three are present together, the mixture is fused, then placed into a beaker glass and dilute H_2SO_4 and some pieces of pure **Zn** added. Zinc reduces the silver and unites with **Cl, Br** and **I**. After 24 hours the solution is decanted, the residue washed with water and the filtrate boiled with excess of Na_2CO_3; this precipitates $ZnCO_3$ and in the filtrate **NaCl, NaBr** and **NaI** may be detected according to § 70 and § 71.

§ 73. **Hydrofluoric acid.** This may be found according to example XV. 4., as soon as the corrosion of a glass tube, in which the substance was heated with concentrated H_2SO_4, has given notice of its presence.

§ 74. **Hydro-fluo-silicic acid.** All salts of H_2SiF_6 are soluble in water excepting those of **K**, and **Ba**, (**Na** salt is difficultly soluble.)

When heated with conc. H_2SO_4 all its salts are decomposed into SiF_4 and **HF**, which attacks the glass of test tubes. When heated in test tube the **dry** salts evolve SiF_4, which when conducted into water gives a gelatinous precipitate of H_4SiO_4 and free H_2SiF_6 dissolves in the water. When heated with an excess of alkaline hydrate the **silico-fluorides** are decomposed into H_4SiO_4 and an alkaline **fluoride.** When melted with Na_2CO_3 they form **NaF** and Na_4SiO_4. Heated with microcosmic salt in the Bunsen lamp no silica skeleton is formed, because all of the silica volatilizes as SiF_4.

§ 75. **Sulphurous and hyposulphurous acids.** When heated with H_2SO_4 the salts of both acids evolve SO_2 gas, recognizable by its odor and by blackening a strip of paper moistened with mercurous nitrate.

SO_2 as well as H_2S blacken $Hg_2(NO_3)_2$, the first by reducing metallic Hg, the second by forming HgS, but H_2S also blackens **lead acetate,** which is not affected by SO_2.

The aqueous solution of an **alkaline sulphite** is acidulated feebly with acetic acid, then $ZnSO_4$ and a little **sodium nitroprusside** are added. The liquid assumes a faint red color, which appears more plainly on adding some yellow ferro-cyanide of potassium; if much SO_2 is present, a purple precipitate is produced. Neutral Fe_2Cl_6 produces in solution of a sulphite a brown-red color, which disappears on heating.

To detect small quantities of H_2SO_3 or $H_2S_2O_3$, some Al, or pure Zn is placed into a testtube with HCl or H_2SO_4, and the substance added. The nascent H reduces the acids and forms H_2S, recognized by odor and by $Pb(C_2H_3O_2)_2$.

Hyposulphurous acid (thiosulphuric). The salts of this acid (excepting BaS_2O_3 and PbS_2O_3) and especially its double salts are quite soluble in water. Its special reactions are detailed in example XXXVII., page 74. In case of simultaneous presence of H_2S, $H_2S_2O_3$ and H_2SO_3, as alkali salts, $ZnSO_4$ is first added to remove H_2S. A portion of the filtrate is tested with HCl, when a precipitate of S with evolution of SO_2 characterizes the **hyposulphurous acid,** while in another portion of the filtrate H_2SO_3 is detected by $Na_2Fe.NO.(CN)_5$.

§ 76. **Chloric acid.** Chlorates are easily detected by their deflagration on charcoal, and the reactions with H_2SO_4, **indigo** and **sulphurous acid** and with **aniline** sulphate as described in example XXXIV., page 45.

When **chlorates** and **nitrates** occur together, the **chlorate** may be recognized by the reduction to **chloride** by heat, which is established by the precipitate of $AgCl$, produced in the acidulated aqueous solution of the fused mass by $AgNO_3$. The **nitric** acid is detected by adding to the substance concentrated solution of $NaOH$ in excess and then some **aluminum** or a mixture of **Zinc** and **iron** in fine subdivision. The reduction of HNO_3 to **nascent hydrogen** produces NH_3. (See example IV. 11).

§77. **Hypochlorous acid.** Salts of $HClO$ (bleaching powder, eau de Javelle, etc.,) have an odor of Cl and bleach indigo and litmus. H_2SO_4 liberates Cl. $CaOCl_2+H_2SO_4=Cl_2+CaSO_4+HO_2$.

Added to solution of $MnSO_4$ they precipitate MnO_2.

$$CaOCl_2+MnSO_4+H_2O=MnO_2+CaSO_4+2HCl.$$

Heating of dry hypochlorites evolves O. When hypochlorites suspended or dissolved in water are heated with a drop of cobaltous nitrate, oxygen is given off.

§ 78. **Nitrous acid.** Heated with concentrated sulphuric acid, **nitrites** evolve brown-red vapors of N_2O_3. Dilute H_2SO_4 evolves NO, which from the air attracts O and forms brown-red vapors of NO_2. The aqueous solution of a **nitrite** acidulated with H_2SO_4 is mixed with a little starchpaste and KI added: the free I colors the starch blue.

A freshly prepared solution of $FeSO_4$ becomes **brown** (from the temporary formation of $2FeSO_4.NO$) by the addition of a **nitrite**, without the addition of H_2SO_4; a **nitrate** only gives this reaction on addition of H_2SO_4.

$$3KNO_2 + FeSO_4 + H_2O = 2NO + KNO_3 + K_2SO_4 + Fe(OH)_2.$$

Nitrous acid is further distinguished from **nitric** acid by its power of reduction. **Nitrites** reduce free metal from solutions of $AuCl_3$ or $Hg_2(NO_3)_2$. Solution of $KMnO_4$ dropped into a **dilute** solution of a nitrite is decolorized as soon as some dilute sulphuric acid is added.

A solution of pure **phenylen-diamine**, $C_6H_4(NH_2)_2$, in dilute sulphuric acid is colored yellow by addition of a nitrite. (A very delicate reaction.)

§ 79. **Boracic acid,** to be detected according to example VIII, 3 and ff.

Molybdic acid. Molybdic trioxide, MoO_3 volatilizes on heating upon charcoal in the oxidation flame. HCl and HNO_3 precipitate it from molybdates, but redissolve it again, if added in sufficient quantity. An acidulated solution of molbydic acid is at first colored blue by H_2S, subsequently dark brown MoS_3 is precipitated, soluble in $(NH_4)_2S$. If Zn is added to a solution of molybdic acid in HCl the color becomes at first blue, then green and lastly brownish-black. If to a solution of molybdic acid $KCNS$ is added, and then HCl and Zn, the solution assumes a carmine color, which may be transferred to ether, if some of it be shaken with the red solution.

If **molybdic trioxide**, MO_3, or a molybdate of an alkali or alkaline earth be heated upon a platinum capsule with some concentrated sulphuric acid, until the latter begins to boil, the H_2SO_4 becomes **blue** as soon as breathed upon.

Its reaction with phosphoric acid is described in example VII., 8.

Tungstic or **wolframic acid.** Wolframic trioxide, $\mathbf{WO_3}$, volatilizes only with difficulty. The acid is precipitated from tungstates by **HCl** or $\mathbf{HNO_3}$; the colorless precipitate of $\mathbf{H_2WO_4.H_2O}$ does **not redissolve** in excess of the acid. By boiling for some time with acids it loses water and becomes **yellow** $\mathbf{H_2WO_4}$. An acidulated solution of tungstic acid is precipitated very slowly by $\mathbf{H_2S}$. But if $\mathbf{NH_4OH}$ and $\mathbf{(NH_4)_2S}$ are added, and then an acid to slight acid reaction, brown $\mathbf{WS_3}$ is precipitated.

A solution of tungstic acid to which **HCl** or, still better, $\mathbf{H_3PO_4}$ has been added becomes blue on addition of **Zn.** If stannous chloride be added to a solution of an alkaline tungstate, a yellow precipitate is thrown down, which becomes blue on warming with **HCl**.

ORGANIC ACIDS.

a. PRELIMINARY TESTS.

§ 80. All salts of organic acids, **oxalates** only excepted, become charred by heating.

As in the case of other acids, it is most advantageous to have only alkaline salts for the detection of organic acids. When it is therefore found that they are combined with other metals, the substance (no matter whether soluble in water, or in acids only), is boiled with excess of $\mathbf{Na_2CO_3}$. The filtrate will contain all of the acids. If necessary it must be concentrated by evaporation and the excess of sodium carbonate is removed by acidulation with **HCl,** and gentle heating to expel $\mathbf{CO_2}$. $\mathbf{NH_4OH}$ is now added to feeble alkaline reaction and then an excess of **calcium chloride.** This will precipitate **oxalic** and **tartaric** acids as $\mathbf{CaC_2O_4}$ and $\mathbf{CaC_4H_4O_6}$. After standing some 15 or 20 minutes the precipitate is separated from the solution by filtration and then each examined separately.

§ 81. **Oxalic acid,** $\mathbf{H_2.C_2O_4}$ and **tartaric acid** $\mathbf{H_2.C_4H_4O_6}$. The precipitate is washed and treated with caustic soda at ordinary temperature. This dissolves the calcium tartrate and leaves the oxalate as residue, which is separated by filtration The filtrate, on being diluted and boiled, will deposit the calcium tartrate again, as a gelatinous precipitate, which redissolves on cooling, if the dilution has not been too great.

§ 82. **Citric acid, $H_3.C_6H_5O_7$.** The filtrate obtained in § 80, is heated to boiling for some time. A precipitate of calcium citrate, $Ca_3(C_6H_5O_7)_2$, is formed, which must be filtered off boiling hot; it must dissolve in HCl and after supersaturation with NH_4OH, must again be deposited on boiling. The filtrate is examined as follows, § 83.

§ 83. **Succinic acid, $H_2.C_4H_4O_4$.** To the filtrate from the calcium citrate a threefold volume of alcohol is added. A precipitate consists of $Ca.C_4H_4O_4$ and must be filtered of and washed with alcohol. The filtrate is examined according to § 84. The calcium succinate readily dissolves in water and on addition of Fe_2Cl_6 gives a brown precipitate of basic ferric succinate $Fe_2(OH)_2.(C_4H_4OH_4)_2$.

§ 84. **Benzoic acid, $H.C_7H_5O_2$.** In the filtrate from the precipitate of calcium succinate by alcohol, **benzoic** acid is precipitated by ferric chloride, as pale yellowish brown, basic ferric benzoate.

§ 85. **Formic acid, $H.CHO_2$,** and **acetic acid, $H.C_2H_3O_2$.** Neither of these acids is precipitated by $CaCl_2$; their normal alkali salts are not precipitated by Fe_2Cl_6 in the cold; they may be distilled with water without decomposition. If no volatile acids are present they may be separated from their salts by distilling with dilute H_2SO_4. The distillate is neutralized by Na_2CO_3 and evaporated to dryness. A portion of the residue is heated in a glasstube with dry As_2O_3, when the odor of kakodyl will indicate the presence of acetic acid. Another portion may be tested with alcohol and sulphuric acid according to example XXV. 12, page 35. Another portion of the residue is dissolved in water and boiled with silver nitrate; a black precipitate of reduced silver indicates formic acid.

b. SPECIAL REACTIONS.

§ 86. **Oxalic acid, $H_2.C_2O_4$.** The reactions of alkaline oxalates are fully described in example XXXVI, page 46. Other oxalates are converted into sodium salt by boiling with Na_2CO_3, or their metallic bases separated by H_2S and $(NH_4)_2S$, and then the same reactions are applied.

§ 87. **Tartaric acid, $H_2.C_4H_4O_6$.** The reactions are described in example VI, page 20. In addition the following: A concentrated **neutral** solution of a tartrate is acidulated with acetic acid and then potassium acetate added, which precipitates cream of tartar. An **acid** solution needs no previous acidulation by acetic acid.

If ammonium **hydrate** be added to a solution of a tartrate, and then a small crystal of silver nitrate and a gentle heat applied, metallic silver will be reduced and adhere to the test tube as a shining silver mirror. A solution of $\mathbf{AgNO_3}$, used in the place of a solid crystal, will also precipitate silver, but in the shape of a black powder. (Formic acid gives the same reaction of reducing silver from its salts).

§ 88. **Citric acid,** $\mathbf{H_3.C_6H_5O_7}$. A solution of free citric acid in water is saturated with lime-water to alkaline reaction. On boiling $\mathbf{Ca_3(C_6H_5O_7)_2}$ is precipitated, but redissolves on cooling. When citric acid or an alkaline citrate is digested with excess of barium acetate, an amorphous precipitate of barium citrate is formed, which becomes crystalline after some hours and shrinks to a small bulk. This behavior distinguishes citric acid from other fruit acids, which are not affected by barium acetate.

§ 89. **Succinic acid,** $\mathbf{H_2.C_4H_4O_4}$. Its calcium and barium salt is soluble in water, but insoluble in alcohol. When the precipitate of basic ferric succinate, described in § 83, is filtered off and washed, it may be tested in a test tube with $\mathbf{NH_4OH}$. Ferric hydrate separates and the ammoniacal solution contains ammonium succinate. When $\mathbf{BaCl_2}$ and alcohol are added, a precipitate of $\mathbf{BaC_4H_4O_4}$ falls.

§ 90. **Benzoic acid,** $\mathbf{H.C_7H_5O_2}$. The free acid is sparingly soluble in water and when concentrated solutions of benzoates are mixed with acids, free benzoic acid precipitates. The reaction with ferric chloride resembles that of succinic acid. The solubility of calcium benzoate in alcohol distinguishes it from the succinate.

§ 91. **Acetic acid,** $\mathbf{H.C_2H_3O_2}$. For reactions with $\mathbf{H_2SO_4}$ and alcohol compare example XXVII. 12. In a neutral solution of an alkaline acetate, $\mathbf{Fe_2Cl_6}$ produces a red color, on boiling a brown precipitate of basic ferric acetate falls, while the solution becomes colorless. (See example XVIII. 18). Silver acetate is sparingly soluble in cold, more readily in hot water.

When dry sodium acetate is heated with dry arsenic trioxide, the penetrating, offensive odor of **kakodyl** (dimethyl-arsine), $\mathbf{As(CH_3)_2}$, is developed.

§ 92. **Formic acid, $H.CHO_2$.** When heated with dilute H_2SO_4 formates evolve free formic acid, recognizable by its pungent odor somewhat resembling acetic acid. Heated with alcohol and concentrated H_2SO_4, formates give off vapor of formic ether (ethyl formate), $C_2H_5.CHO_2$, which has a strong flavor of arrack. When a dry formate is heated with concentrated H_2SO_4, CO is evolved. $H.CHO_2=CO+H_2O$. Silver nitrate produces in an aqueous solution of a formate a white precipitate of silver formate, $AgCHO_2$, which blackens on heating with deposition of metallic silver. $2AgCHO_2=2Ag+CO_2+HCHO_2$. If free NH_4OH is added to a solution of an alkaline formate and a **crystal** of $AgNO_3$, and heat applied gently, the reduction of silver takes place with formation of a metallic mirror.

When formic acid, or an alkaline formate, is heated after addition of $HgCl_2$, calomel precipitates, which if formic acid is in sufficient quantity, will be farther reduced to metallic mercury.

Boiling with excess of mercuric oxide will destroy all the formic acid in a mixture, while acetic and other volatile acids remain undecomposed.

Ferric chloride reacts with formic acid, as with acetic acid.

When both acetic and formic acids are present in the same substance, the first is recognized by the kakodyl reaction, the formic acid by the reduction of silver and mercury. Lead formate is sparingly soluble in water, insoluble in alcohol. Lead acetate is easily soluble in both.

ANALYSIS OF SILICATES.

The presence of silica is recognized during the preliminary examination by the skeleton produced in the microcosmic bead. See example XXXV., 4. Some silicates are decomposed by mineral acids wholly or in part, others remain unaffected by them.

§ 93. **Silicates decomposed by acids.** (Soluble glass, zeolites, slags, etc.) The substance is converted into very fine powder (by first crushing in a steel mortar and then grinding in an agate mortar) and digested with concentrated HCl (or HNO_3) at a temperature near to boiling water. It is constantly stirred with a rounded glass rod until all feeling of grittiness disappears, which indicates the completion of the decomposition. Water is then added, and the mixture evaporated to dryness.

The dry residue is moistened with **HCl** and heated. This serves to convert the gelatinous soluble silicic acid into insoluble silica. Water is now added, and after boiling, $\mathbf{SiO_2}$ is separated by filtration. The filtrate contains the bases, which had been united with silicic acid, as chlorides, to be separated in the usual manner. Pure $\mathbf{SiO_2}$ must dissolve completely by protracted boiling, with $\mathbf{Na_2CO_3}$; titanic acid, which is sometimes present, does not dissolve.

Some silicates which resist decomposition by **HCl** or by $\mathbf{HNO_3}$ yield to protracted heating with moderately concentrated sulphuric acid.

§ 94. **Silicates not decomposed by acids.**

a. **Separation of $\mathbf{SiO_2}$.** The finely powdered substance is mixed with its fourfold weight of anhydrous $\mathbf{Na_2CO_3}$ and fused in a platinum crucible over a powerful lamp until the mass becomes thoroughly fluxed and flows quietly. (On a small scale this operation may be performed before the blowpipe on a piece of platinum foil bent into a somewhat hollow shape). The fluxed mass is treated with **HCl**, the acid liquid evaporated to dryness, without previous filtering, and the dry residue heated with some concentrated **HCl**, to convert insoluble oxychlorides, formed during the evaporation, into soluble chlorides. Water is now added and after boiling silica is separated by filtration, and the bases detected in the filtrate.

§ 95. b. **Detection of the alkalies.** In a platinum crucible an intimate mixture is made of 1 part of the powdered silicate and 5 parts of pure $\mathbf{CaF_2}$, with enough concentrated $\mathbf{H_2SO_4}$ to form a paste. The mixture is heated very slowly and gradually until all excess of $\mathbf{H_2SO_4}$ is expelled. The dry mass is repeatedly boiled out with water; from the filtered solution sulphuric acid is removed by $\mathbf{BaCl_2}$ and without filtering sufficient milk of lime ($\mathbf{Ca(OH)_2}$ mixed with water to a thin paste) is added to alkaline reaction. The mixture is boiled, filtered, barium and calcium precipitated, as carbonates, by $\mathbf{NH_4OH}$ and $\mathbf{(NH_4)_2CO_3}$ and the alkalies detected as directed in § 1 and ff.

§ 96. **Fluorine.** Silicates containing **F**, when treated with concentrated sulphuric acid, evolve $\mathbf{SiF_4}$, which does not corrode glass. But if a glass rod, to which a drop of water adheres, is held over the mixture evolving the gas, the water becomes coated with a pellicle of $\mathbf{SiO_2}$.

In this case the finely powdered dry substance is placed into a small flask fitted with a bent glass tube, which dips into a test-tube half filled with distilled water. The flask and bent glass-tube must be scrupulously clean and dry. A mixture of concentrated $\mathbf{H_2SO_4}$ with an equal volume of fuming $\mathbf{H_2SO_4}$ is poured upon the substance and heat applied, first gently, then to the beginning volatilization of the sulphuric acid. The gas escapes through the water of the testtube and is there decomposed into silicic and hydro-fluo-silicic acid (see example XV. 5.) After the completion of the operation the liquid in the testtube is supersaturated with $\mathbf{NH_4OH}$, the silica filtered off, and the filtrate evaporated in a platinum dish, on the water bath. The dry residue is examined for alkalies according to § 2.

Or else the fluxed silicate, obtained according to § 94, is exhausted with water. The solution, containing **all** of the acids present in the silicate, ($\mathbf{H_3BO_3}$, **HF**, $\mathbf{H_4SiO_4}$, $\mathbf{H_4TiO_4}$, etc.,) is slightly acidulated with **HCl**. An excess of hydrochloric acid must be avoided, as $\mathbf{CaF_2}$, which is to be formed, is somewhat soluble in the salts of ammonium, especially ammonium fluoride. Heat is applied to expel $\mathbf{CO_2}$, and $\mathbf{NH_4OH}$ added to alkaline reaction. The precipitate of silica, alumina, etc., is separated by filtration and $\mathbf{CaCl_2}$ added, which precipitates **F** as $\mathbf{CaF_2}$ to be examined according to example XV. and § 73.

Calcium fluoride is not decomposed by fluxing with $\mathbf{Na_2CO_3}$, unless silica is also present in the mineral, or is added for the purpose.

§ 97. **Titanic acid, $\mathbf{H_4TiO_4}$.** In silicates titanic acid frequently occurs and is partly separated with the silicic acid, partly with iron and alumina.

a. Separation of **titanic** and **silicic** acids occurring together (with $\mathbf{BaSO_4}$, $\mathbf{SrSO_4}$, $\mathbf{Al_2O_3}$, etc.) The titaniferous silica is boiled for some time with some strong sulphuric acid until the latter begins to volatilize. The mass is cooled and poured into an excess of water, drop by drop, to avoid heating. It is then filtered, the free acid of the filtrate somewhat, but not entirely, neutralized with caustic soda, and the solution, (yet acid) boiled for some time. Metatitanic acid precipitates.

Or else the titaniferous silicate is repeatedly evaporated in a platinum crucible with a mixture of **HF** and **HCl**. By this proceeding **Si** is expelled and the residue can only contain **Ti,** and such insoluble substances, as $BaSO_4$, Al_2O_3. SnO_2, Cr_2O_3, or others which, like Al_2O_3 and SnO_2 resist decomposition by $\mathbf{Na_2CO_3}$. The residue is melted in a crucible with $\mathbf{KHSO_4}$ and the fused mass treated with cold $\mathbf{H_2O}$. This leaves the insoluble $\mathbf{BaSO_4}$ and $\mathbf{SrSO_4}$ behind. The filtrate is boiled for some time: metatitanic acid precipitates, while alumina and traces of **Ti** remain in solution.

b. Separation of **titanic acid** from **alumina** and **iron.**

The precipitate of iron, containing titanic acid, is dissolved in dilute sulphuric acid, nearly neutralized with caustic soda and to the slightly acid solution a few drops of nitric acid and some water are added and boiling heat applied for some time. Titanic acid becomes insoluble and precipitates as metatitanic acid.

Titanium gives with microcosmic salt in the oxidation flame a bead which is yellow, while hot, colorless when cold. In the reduction flame, especially on addition of a little tinfoil, the bead is yellow while hot, violet when cold. If iron be present, the bead will appear red, yet, even then, a sufficient addition of tinfoil will produce a violet bead. In silicates it is almost impossible to detect titanium by the blow-pipe.

An acid solution of a titanate is colored blue on addition of metallic zinc; from this ammonium hydrate precipitates blue $\mathbf{Ti_2O_3}$. When precipitated titanic acid is treated by zinc and hydrochloric acid, it is also colored blue.

ANALYSIS OF CYANIDES.

§ 98. Of the simple cyanides only those of the alkalies and $\mathbf{Hg(CN)_2}$ are soluble in water. **All cyanides,** not even excepting **AgCN,** when heated with concentrated **HCl,** give off free **HCN,** recognizable by its odor of bitter almonds, and are therefore detected during the solution of the substance. Some **double cyanides** (e. g. red or yellow prussiate of potash) give off only a part of their **CN** as **HCN** on addition of **HCl.**

All cyanides, with the exception of those of the alkali metals, are decomposed on ignition.

§ 99. In **alkaline** cyanides **CN** is detected according to example XLII. 3. To detect it according to the same process in mercuric cyanide, it is necessary to decompose the salt by $\mathbf{H_2S}$; for $\mathbf{AgNO_3}$ will not give a precipitate of $\mathbf{AgCN}$ in a solution of $\mathbf{Hg(CN)_2}$.

$\mathbf{AgCN}$ is decomposed at red heat, while $\mathbf{AgCl}$, $\mathbf{AgBr}$, $\mathbf{AgI}$ are not.

To detect cyanogen in the rest of the simple or double cyanides, it is best to distill them with $\mathbf{HCl}$. $\mathbf{HCN}$ distils over and the distillate is saturated with $\mathbf{NaOH}$ and then treated according to example XLII. 3. Or the dry cyanides are fused in a porcelain crucible with $\mathbf{Na_2CO_3}$, the fused mass extracted with $\mathbf{H_2O}$ and $\mathbf{CN}$ detected in the solution containing $\mathbf{NaCN}$.

§ 100. **Free hydrocyanic acid** does not produce at once a precipitate of prussian blue in a mixture of ferrous and ferric salts as directed in example XLII. 3. The addition of an excess of $\mathbf{NaOH}$ is requisite, to produce a ferro-cyanide, when the mixture is heated. $\mathbf{2HCN+2NaOH+FeSO_4=Fe(CN)_2+Na_2SO_4+2H_2O}$. $\mathbf{Fe(CN)_2+4NaCN=Na_4Fe(CN)_6}$.

The addition of $\mathbf{NaOH}$, at the same time, precipitates $\mathbf{Fe(OH)_2}$ and $\mathbf{Fe_2(OH)_6}$. Both of these precipitates dissolve when $\mathbf{HCl}$ is added and the $\mathbf{Fe_2Cl_6}$ thus formed, then reacts with the ferro-cyanide.

In the solution of ferric chloride $\mathbf{KCN}$ produces a precipitate of $\mathbf{Fe_2(OH)_6}$.

$$\mathbf{6KCN+Fe_2Cl_6+6H_2O=Fe_2(OH)_6+6KCl+6HCN.}$$

Traces of free hydrocyanic acid or of alkaline cyanides may be detected by converting the $\mathbf{HCN}$ into $\mathbf{NaCN}$ by addition of $\mathbf{NaOH}$ and then proceeding as directed in example XLII. 5.

§ 101. Double cyanides insoluble in water, such as prussian blue, are decomposed most readily by boiling with $\mathbf{NaOH}$. The insoluble part contains the bases, which are separated as usual, while the filtrate contains sodium ferro-cyanide and ferri-cyanide, together with those bases which are soluble in sodium hydrate. To test for ferro-cyanides or ferri-cyanide it is necessary to remove these bases (**Pb**, **Zn**, **Al**, etc.) by $\mathbf{H_2S}$. The precipitate is removed by filtration, the filtrate acidulated with $\mathbf{HCl}$ and $\mathbf{H_2S}$ again added to remove $\mathbf{PbS}$ etc. The precipitate is again filtered off, an excess of $\mathbf{H_2S}$ removed by heat and the filtrate tested by $\mathbf{Fe_2Cl_6}$, which precipitates prussian blue. For even if a ferri-cyanide had been present, it would have been converted by $\mathbf{H_2S}$ into a ferro-cyanide.

When Turnbulls blue is heated with **NaOH** it is decomposed into **$Fe(OH)_2$** and **ferri-cyanide.**

If **oxidizing** substances are present during the heating of a **ferro-cyanide** with **NaOH,** there is a conversion into **ferri-cyanides** while on the other hand the **red** prussiate is converted into the **yellow** by the presence of **reducing** substances.

§ 102. If only the **metals** combined with **CN** are to be detected, the substance may be heated with a mixture of 3 parts concentrated sulphuric acid and 1 part of water, until the excess of sulphuric acid is again driven off. The residue is then dissolved in **HCl** and tested by the usual method. By such treatment the alkalies may be found, which are contained in some of the insoluble double cyanides, from which neither water, nor dilute acids are capable to extract them.

EXAMPLES FOR PRACTICE IN ANALYSIS OF ORGANIC SUBSTANCES.

Organic substances have, as their constituents, only a very limited number of elements: **C, H, O,** and **N** occurring most frequently. They differ in the number of atoms of these few elements and in their relative grouping within the molecule. They cannot therefore be distinguished qualitively in the same manner as inorganic substances, by the special reactions of their elements. We have to observe their physical properties; odor, taste, volatility, and especially melting and boiling temperatures are of great importance, and in the majority of cases, ultimate quantitative analysis, by the combustion method, must be resorted to.

Only a limited number of organic bodies contain groups of atoms, which show special reactions and from these the following examples are selected. Some of these reactions are common to several substances. Thus the reduction of cupric to cuprous salts is not only a property of some sugars, but shared by chloroform and other compounds, the production of the blue oxide ot molybdenum from the acid or the reduction of metallic silver from its salts is, in like manner, effected by several substances, and very few of the reactions given below can, singly and unsupported by others, be relied upon for identification of any substance. It is only by the concurrence of several reactions together with the observations of the physical properties, that we may safely determine the presence or absence of a certain compound. Hence short descriptions precede the reactions given below.

1. ALCOHOL. $C_2H_5.OH$.

Ethylic Alcohol.

Officinal alcohol of the U. S. P. contains 94 per cent by volume, of ethyl alcohol and 6 per cent of water. It is a transparent, colorless, volatile liquid, of peculiar odor and burning taste, of specific gravity 0.82. It boils at 78° C. and is readily inflammable, burning with a blueish, non-luminous flame. It mixes with water in all proportions. It dissolves many substances, and forms, with some, definite compounds called alcoholates.

Absolute alcohol has spec. grav. 0.7937, and boils at 73.4° C.

1. In a testtube mix about 1 C.C. of solution of $K_2Cr_2O_7$ with one fourth the quantity of H_2SO_4 and dilute with 2 or 3 C.C. of water. Now add 1 C.C. of alcohol, mix and heat gently. The liquid will become green from the formation of chromic alum while **aldehyde** C_2H_3OH will volatilize, easily recognized by its odor.

$$3C_2H_5OH+K_2Cr_2O_7+4H_2SO_4=3C_2H_3OH+K_2SO_4.Cr_2(SO_4)_3+7H_2O.$$

2. Mix in a testtube about 1. C.C. each of H_2SO_4 and C_2H_5OH. heat to boiling and again add the same quantity of alcohol on heating, **ether,** $(C_2H_5)_2O$, is formed, whose odor is easily detected. The reaction occurs in two stages. First **acid ethyl sulphate** (ethyl-sulphuric acid), $C_2H_5.H.SO_4$, is formed, and then with more alcohol, **ethylic ether** and sulphuric acid.

a. $C_2H_5.OH+H_2SO_4=C_2H_5.H.SO_4+H_2O.$

b. $C_2H_5.H.SO_4+C_2H_5.OH=(C_2H_5)_2O+H_2SO_4.$

3. Mix in a testtube equal volumes (about 1 C.C. each) of **alcohol, sulphuric acid** and a saturated solution (or a crystal) of **sodium acetate.** Apply heat and there will be formed **ethyl acetate** (acetic ether), $C_2H_5.C_2H_3O_2$, whose fruity odor will be easily recognized. Acid ethyl sulphate is first formed and this decomposes with sodium acetate into acid sodium sulphate and ethyl acetate.

$$C_2H_5.H.SO_4+NaC_2H_3O_2=C_2H_5.C_2H_3O_2+NaHSO_4.$$

4. Into 2 C.C. **alcohol** put a small crystal of **iodine** and dissolve it at a gentle heat. Now add drop by drop a solution of **KOH**, until the brown color of the solution disappears. At once a copious yellow precipitate of **iodoform,** CHI_3, falls down, well characterized by its odor, while potassium iodide and potassium formate are in solution.

$$C_2H_5.OH+6KOH+I_8=CHI_3+CHO_2K+5KI+5H_2O.$$

5. To a small quantity of molybdic acid, dissolved in concentrated H_2SO_4 and heated, add cautiously in a testtube a

few drops of alcohol. A violent ebullition will occur, accompanied by the formation of aldehyde, while the liquid is colored green. When agitated, so that small drops will adhere to the sides of the testtube, these will quickly become deep blue, and on standing, the same color will develop in the whole liquid, from the reduction of the molbydic acid to $\mathbf{MoO_2}$.

Many substances besides alcohol are capable of reducing molybdic acid.

2. CHLOROFORM. $CHCl_3$.

Officinal chloroform of the U. S. P. is a heavy, colorless, volatile liquid, of peculiar odor, sweet, burning taste and spec. grav. 1.49. It boils at 60° to 61° C. It is soluble is 200 parts water, miscible in all proportions with alcohol and ether. Its reaction, when pure, is neutral to test papers. The U. S. P. permits the presence of one per cent alcohol, which helps to preserve the chloroform from decomposition.

1. Dip a narrow strip of paper into chloroform and ignite at the lamp flame. The flame has a geeen mantle and emits fumes of $\mathbf{HCl}$, shown by reddening a strip of moistened blue litmus paper, held near the flame, and by the white fumes produced, when a drop of ammonia is brought near it on a glass rod.

2. Silver nitrate does **not** produce a precipitate of $\mathbf{AgCl}$ with **pure** chloroform. But when chloroform has been exposed to light and heat for some time, especially if no alcohol is present, various decompositions take place, and chlorinated substances are formed, which yield a precipitate with $\mathbf{AgNO_3}$.

3. To a dilute solution of $\mathbf{NaOH}$ add a drop of solution of $\mathbf{CuSO_4}$, then a drop of chloroform and heat. The **blue cupric** hydrate, precipitated at first; is reduced to **red cuprous** oxide. If too much cupric sulphate is taken in proportion to the chloroform, some of the blue hydrate is not reduced but converted into black $\mathbf{CuO}$ by heating. Addition of a little alcohol facilitates the solution of chloroform in aqueous solutions, and thereby hastens the reaction. For detecting small quantities alcoholic solution of $\mathbf{NaOH}$ or $\mathbf{KOH}$ is preferable.

4. Heat some chloroform with solution of $\mathbf{KOH}$, to which some alcohol may be added. The chloroform is thereby decomposed into $\mathbf{KCl}$ and potassium formate, $\mathbf{K.CHO_2}$.

$$CHCl_3+4KOH=3KCl+KCHO_2+2H_2O.$$

Dilute the solution and divide into two portions. Acidulate one portion with $\mathbf{HNO_3}$ and boil. The potassium formate is decomposed and $\mathbf{KNO_3}$ and **KCl** remain in solution. Solution of $\mathbf{AgNO_3}$ now produces a copious precipitate of **AgCl,** thus showing the presence of chlorine in chloroform.

5. The second portion of the solution of **KCl** and $\mathbf{K.CHO_2}$ (4.) is cooled, some $\mathbf{NH_4OH}$ is added and then a small crystal of $\mathbf{AgNO_3}$. Heat gently and a mirror of metallic silver will adhere to the bottom of the testtube, produced by the reducing action of the formic acid. (Compare systematic course, organic acids, § 92.)

6. *Hofmanns test.* To some alcoholic solution of **KOH** add a drop of **aniline** $\mathbf{C_6H_5.NH_2}$, and then one of chloroform. At once, or, if the solution is very dilute, on heating, a peculiar, penetrating, offensive odor of **benzo-isonitril** (phenyl isocyanide) $\mathbf{C_6H_5.NC}$ is perceived, which enables the recognition of very minute quantities of chloroform. All substances, whose decomposition by caustic alkalies produces chloroform, give the same reaction.

$$\mathbf{CHCl_3+3KOH+C_6H_5.NH_2=C_6H_5.NC+3KCl+3H_2O}.$$

3. CHLORAL HYDRATE. $\mathbf{C_2HCl_3O.H_2O}$.

Chloral hydrate forms transparent, colorless, rhombic crystals (or crystalline crusts), volatile, of peculiar, pungent, aromatic odor, acrid taste and neutral reaction. Soluble in 1½ parts water, in 4 parts chloroform, and freely in alcohol and ether. It melts at 58° C; decomposes into anhydrous chloral, and water at 78° C., and boils at 95° C. When pieces of chloral hydrate are shaken with solid camphor, they liquify.

1. To some solution of chloral hydrate in water, add **KOH** solution and boil. Vapor of chloroform is evolved, recognized by its odor, while potassium formate remains in solution.

$$\mathbf{C_2HCl_3O.H_2O+KOH=CHCl_3+KCHO_2+H_2O}.$$

Other alkaline hydrates, as well as lime or baryta water have the same effect as **KOH.**

2. The chloroform obtained by decomposition of chloral hydrate may be distilled off and examined separately or Hofmann's test (2, 6) may be applied to the mixture of chloroform and potassium formate obtained above (1).

3. After removal of the chloroform, by boiling the solution of chloral treated with **KOH**, the presence of potassium formate may be proven by adding some **NH_4OH**, and then a crystal of silver nitrate, and heating, when a silver mirror will be formed.

4. To a small quantity of aqueous solution of chloral hydrate, diluted with water, add a few drops of ammonium sulphide. A deep brown-red color is produced in the solution, which on standing, becomes turbid and deposits a copious brown-red precipitate. Addition of acetic acid hastens the precipitation and develops a peculiar penetrating odor.*

5. The reduction of cupric salts to cuprous takes place in presence of chloral hydrate under the same conditions as in case of chloroform, (2, 3) or of glucose (4, 2).

4. GLUCOSE. $C_6H_{12}O_6+H_2O$.

Grape-sugar

Granular, crystalline solid, soluble in its own weight of water, sweetish taste, slightly soluble in alcohol, from which it crystallizes in anhydrous prisms. Melts at 86° C. when hydrated (at 146° C. anhydrous). Found in dried fruits, honey, in diabetic urine, artificially prepared from starch and used for adulteration of cane-sugar. With yeast, its solution ferments, forming alcohol and **CO_2**. In concentrated sulphuric acid it dissolves without blackening. Turns the plane of polarized light to the right. It forms crystallized compounds with **$NaCl$** and other salts, when heated to 170° C. it melts and forms colorless glucosan, **$C_6H_{10}O_5$**, and at higher temperature brown caramel. Glucose is especially characterized by its reducing action, resembling the aldehydes.

1. To an aqueous solution of glucose add **KOH**, on heating the colorless solution becomes first yellow, then brown. *(Moore's test).*

2. To an aqueous solution of glucose add a few drops of dilute solution of **$CuSO_4$**, then **KOH** or **$NaOH$** (not **NH_4OH**) in excess. The blue precipitate of **$Cu(OH)_2$**, first formed redissolves

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* This reaction may be modified so as to detect sulphuretted hydrogen (and soluble sulphides) and also minute traces of ammonia.

To detect **H_2S** the reagent is made by mixing an aqueous solution of chloral with ammonia water. Even a small quantity of **H_2S** or a soluble sulphide, added to this, produces a brown red color.

Traces of ammonia are found by mixing chloral hydrate in aqueous solution with freshly prepared sulphuretted hydrogen water and adding it to the liquid containing ammonia. A single drop of ammonia water in a litre of distilled water will give a distinct yellow color.

when more **KOH** is added. Heat the clear blue solution, at first an orange cloud of **$Cu_2(OH)_2$** will rise to the top and on further heating, red **Cu_2O** will be formed throughout the solution.* *(Trommer's test).*

3. To the aqueous solution of glucose add some **Na_2CO_3** and and then white **bismuth subnitrate, $BiNO_3$ $(OH)_2$.** Heat and the reduction of **Bi** to the metallic state will blacken the white salt. *(Boettgers test.)*

4. A dilute solution of **picric acid, $H.C_6H_2(NO,)_3O$,** added to an alkaline solution of glucose, produces a deep red color, due to the formation of **picramic acid, $H.C_6H_2.NH_2.(NO_2)_2O$.** By employing a solution of standard strength, (centi-normal= 2, 29 grammes picric acid to 1 litre water) a comparison of the depth of the color with that of specimens of known strength, permits an approximate estimation of the quantity of glucose present. The same reaction is shown in milk sugar, fruit sugar and maltose, but not by cane sugar.

5. CANESUGAR. $C_{12}H_{22}O_{11}$.

Saccharose.

A colorless solid, crystallizing in monoclinic prisms, of sweet taste, soluble in 0.5 parts of water, in 175 parts of cold alcohol, U. S. P., in 80 parts boiling absolute alcohol, insoluble in ether. Its spec. grav. is 1.6. At 160° C it fuses into a colorless liquid, which becomes brown at higher temperature, forming caramel. Sugar combines with bases (calcium, barium, strontium, iron, lead, etc) forming saccharates. It does not ferment with yeast, until changed into other varieties of sugar.

1. Upon a small piece of cane sugar put a drop or two of concentrated sulphuric acid. The sugar will rapidly become charred. Even if dilute solutions of sugar and **H_2SO_4** are heated gently together this blackening will occur. (Compare example XLIV. 2.

2. Pure cane sugar does **not** give the reactions of glucose with alkaline copper solution or with picric acid.

3. Dissolve a small piece of cane sugar in water, add a few drops **HCl** (or of other acid) and boil. The cane sugar is thereby **inverted,** that is changed into glucose and fruitsugar

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* The modification of this test by Fehling, to adapt it to quantitative determinations, is given among the examples for volumetric analysis further on.

(levulose). The solution will now give all the reactions of glucose enumerated in No. **4.** This change depends upon the appropriation of 1 molecule of water by the cane sugar.

$$C_{12}H_{22}O_{11}+H_2O=(+)C_6H_{12}O_6+(-)C_6H_{12}O_6$$

The two sugars resulting from the splitting up of cane sugar turn polarized light in opposite directions and are therefore marked (+) $C_6H_{12}O_6$, glucose, turning to the right, and (−) $C_6H_{12}O_6$, levulose, turning to the left.

Both of these sugars are fermentable, while unchanged cane sugar is not.

6. PHENOL. C_6H_5OH.

Carbolic acid.

Colorless crystals, of peculiar odor, burning taste, melting at 42° C. when anhydrous, (at a lower degree when containing water) boiling at 181° C. With a small quantity of water it deliquesces, but requires 20 parts of water for complete solution. Very soluble in alcohol, ether, chloroform, glycerine and oils. On standing most commercial varieties assume a red color. It is poisonous.

1. Make a very dilute aqueous solution of phenol and add a drop of nitric acid. On heating the liquid will assume an intense yellow color, due to the formation of **picric acid,** $C_6H_2(NO_2)_3OH$. (Tri-nitro-phenol).

2. To the aqueous solution of phenol add bromine water. A white flocculent precipitate of **tri-brom-phenol,** $C_6H_2Br_3OH$, falls, even in very dilute solutions. The precipitate redissolves on addition of **KOH.** Many other substances give similar precipitates with bromine water.

3. To the aqueous solution of phenol add a drop of pure ferric chloride solution. A violet blue color will result. Free acids and several salts interfere with the reaction.

4. To a very dilute aqueous solution of phenol add a few drops of mercurous nitrate and potassium nitrite. The solution assumes a red color and metallic mercury precipitates. Salicylic acid gives the same reaction.

5. Dip a fresh-cut shaving of pine wood into a solution of phenol and lay aside to dry. After a little time steep the same in hydrochloric acid. In about half an hour the chip will be colored blue.

7. ALKALOIDS.

GENERAL PROPERTIES AND REACTIONS.

Alkaloids are organic bases, containing nitrogen, mostly derived from vegetable, some from animal sources. Their constitution is supposed to be that of **amines,** i.e. NH_3 whose **H** has been wholly or in part replaced by **C** and **H** sometimes combined with **O,** either grouped as alcohol radicles, or, more often of unknown composition.

Those free from **O** are volatile, those containing **O** cannot be distilled without decomposition. Most of them are sparingly soluble in water, quite soluble in alcohol, and mostly in ether and chloroform, of bitter taste and give alkaline reactions with testpapers. In the formation of salts with acids and in their general behavior with reagents they bear great resemblance to ammonia.

From their salts they are liberated by caustic alkalies. From acid solutions they are mostly precipitated by the following reagents:

Iodine dissolved in potassium iodide.

Mercuric potassium iodide, white or yellow precipitates.

Bismuth potassium iodide, orange precipitates (does not affect Digitaline, Narceine, Solanine, Veratrine).

Cadmium potassium iodide, colorless and crystalline.

Platinic chloride, yellow or gray.

Gold chloride, yellow.

Mercuric chloride.

Phospho-molybdic acid.

Phospho-wolframic (-tungstic) **acid.**

Meta-wolframic (-tungstic) acid.

Phospho-antimonic acid.

Picric acid.

Tannic acid.

With few exceptions (strychnine, cinchonine. narcotine,) their precipitation is interfered with by the presence of tartaric acid. They form salts with acids, not by replacing their hydrogen as the metallic bases do, but like ammonia, by uniting with the acids, retaining their hydrogen.

Thus $K_2+(HCl)_2=2KCl+H_2$; while $NH_3+HCl=NH_4Cl$, ammonium chloride.

Morphine, $C_{17}H_{19}NO_3.H_2O + HCl + 2H_2O$ = morphine hydrochlorate, $C_{17}H_{19}NO_3.HCl + 3H_2O$.

Or Quinine $C_{20}H_{24}N_2O_2,3H_2O + H_2SO_4 + 4H_2O$ = sulphate of quinine, $C_{20}H_{24}N_2O_2.H_2SO_4 + 7H_2O$.

A number of alkaloids are very poisonous even in small doses.

Non-volatile alkaloids may be subdivided into 3 groups.

First group. Alkaloids precipitated by **KOH** or **NaOH** from the solution of their salts, and redissolved by excess of precipitant: **Morphine**, etc.

Second group. Alkaloids precipitated by **KOH** or **NaOH** and **not** redissolved by excess of precipitant, and also precipitated by **$NaHCO_3$** from moderately concentrated acid solution. **Narcotine, Quinine, Cinchonine,** etc.

Third group. Alkaloids precipitated by **KOH** or **NaOH** and **not** redissolved by excess of precipitant; not precipitated by **$NaHCO_3$** from moderately concentrated acid solution: **Strychnine, Brucine, Veratrine, Atropine,** etc.

Very recently the detection of the poisonous vegetable alkaloids has been rendered more difficult by the discovery, that bodies of similar reaction are formed in decomposing animal matter. These have been called: **Ptomaines** or **Septicines** and were for a while supposed to be distinguishable by their reduction of potassium ferri-cyanide to ferro-cyanide. It has been found however, that this reduction is also effected by vegetable alkaloids to a greater extent than was formerly supposed, and thus distinguishing reactions must still be sought for and the whole subject more thoroughly investigated.

8. Morphine. $C_{17}H_{19}NO_3 + H_2O$.

One of the opium alkaloids; very poisonous. From alcoholic solution it crystallizes in colorless, shining prisms, precipitated from its salts, it forms a white powder, inodorous, of bitter taste, alkaline reaction; soluble in 500 parts boiling, sparingly in cold water, readily soluble in alcohol, nearly insoluble in ether or chloroform. Heated on platinum foil it loses water, fuses, and then chars, and burns without residue. It forms crystallizable salts with acids, which dissolve readily in water and in alcohol, but are insoluble in ether and in amylic alcohol.

1. Put into a watch glass a drop of strong nitric acid and throw upon it a little solid morphine sulphate, it will assume a deep orange color, gradually fading to yellow.

2. From an aqueous solution of morphine sulphate a solu-

tion of **KOH** or **NaOH** added drop by drop, precipitates morphine, the precipitate redissolves when an excess or **KOH** is added.

3. **NH_4OH**, or an alkaline **carbonate** or bicarbonate precipitates morphine, but does not redissolve it if added in excess.

4. A few drops of solution of **pure, neutral Fe_2Cl_6** added to a neutral solution of morphine sulphate produce a deep blue color. If too much **Fe_2Cl_6** is used its yellow color will render the solution green.

5. Prepare a solution of **cuprammonium sulphate** by adding **NN_4OH** to some solution of **$CuSO_4$** until the precipitate is redissolved. Divide the solution into two parts, to one add a little solution of morphine salt, to which a few drops of **NH_4OH** have been added. Heat both to boiling and compare the colors by transmitted light. The tube containing the morphine will be greenish blue while the other will have its blue color unchanged. Very small quantities of morphine will suffice to produce this reaction.

9. Quinine $C_{20}H_{24}N_2O_2+3H_2O$.

One of the alkaloids of cinchona bark. A white powder, inodorous, very bitter, has alkaline reaction. Soluble in 1600 parts of cold in 700 parts of boiling water; in 6 parts of cold and 2 parts of boiling alcohol, soluble in ether, chloroform and glycerine. Melts at 57°C, at 100° loses water, at higher temperature it burns without leaving a residue. It dissolves readily in dilute acids.

1. To an aqueous solution of quinine sulphate add **H_2SO_4** and hold into bright sunlight, or condense the solar rays in the solution by a lens. A bright blue fluorescence occurs. (This is also produced by quinidine sulphate, but not by cinchonine or cinchonidine.)

2. **KOH, NaOH, NH_4OH** and their carbonates precipitate quinine from the aqueous solution of its salts, the precipitate is almost insoluble in excess of **KOH** or **NaOH**, but dissolves somewhat in excess of **NH_4OH**.

3. To an aqueous solution of a quinine salt add freshly prepared **chlorine-water** and then some **ammonia water:** An emerald green precipitate of **thalleioquine** results, soluble with green color in more **NH_4OH.**

4. To an aqueous solution of a quinine salt add first chlorine water, then potassium ferro-cyanide and lastly a few drops of NH_4OH **are** added, a deep red color results, changing soon to dirty brown.

10. Cinchonine. $C_{20}H_{24}N_2O$.

A cinchona alkaloid, forming colorless, prismatic crystals, having but little taste; almost insoluble in water, hot or cold; soluble in 110 parts cold and in 28 parts hot alcohol, very slightly soluble in ether or chloroform readily soluble in dilute acids. Melts at 250° C., above that it darkens and partially sublimes. It burns without residue. Its sulphate does not fluoresce. Its ferro-cyanide forms characteristic crystals, when observed under the microscope.

1. When chlorine water is added to a solution of a cinchonine salts no green color results from addition of ammonia, but a yellowish-white precipitate, insoluble in excess of ammonia.

2. With the caustic alkalies and their carbonates and bicarbonates cinchonine salts form similar precipitates as quinine, insoluble in excess.

11. Strychnine. $C_{21}H_{22}N_2O_2$.

A poisonous alkaloid of nux vomica and other strychnos varieties. It forms colorless crystals, inodorous, excessively bitter, has alkaline reaction. Soluble in 6700 parts of cold and in 2500 parts of boiling water, more soluble in officinal alcohol and chloroform, insolnble in ether or absolute alcohol. Easily soluble in dilute acids. Its neutral salts react alkaline.

1. Into a shallow porcellain dish put a small crystal of strychnine and a drop of H_2SO_4. Then place into the liquid a small crystal of potassium dichromate. On inclining the dish, so as to let the acid flow about, streaks of deep blue color will flow from the crystal of strychnine, passing through the shades of violet into red color and fading into a deep yellow. Manganese dioxide, potassium permaganate and other oxidizing agents may be used instead of the potassium dichromate.

2. KOH produces in an aqueous solution of a strychnine salt a white precipitate of strychnine. This is insoluble in excess of the precipitant.

3. **$NaHCO_3$** produces no precipitate in acid solution of strychnine; from neutral solution a precipitate falls, which is redissolved by addition of a drop of acid. After standing 24 hours strychnine will separate in crystals.

4. **Chlorine water** produces even in dilute solutions of strychnine a white precipitate, soluble in ammonium hydrate.

5. **HNO_3** dissolves **strychnine** to a colorless liquid. But if **brucine** be present, (which is sometimes present as an impurity) a red color, fading to yellow, is produced.

12. ATROPINE. $C_{17}H_{23}NO_3$.

An alkaloid prepared from Atropa Belladonna. Odorless crystals, permanent in air, of bitter and acrid taste and alkaline reaction. Melts at 90°C and sublimes at 140°C. Soluble in 600 parts water at 15°C and in 35 parts of boiling water; easily soluble in alcohol and chloroform, much less in ether. With acids it forms salts, which are quite soluble in water and alcohol, almost insoluble in ether. They crystallize with difficulty. Even very minute quantities of atropine or its salts dilate the pupil strongly.

1. Heat a small quantity of an atropine salt with some concentrated sulphuric acid. No change of color occurs. An aromatic odor arises, resembling a mixture of orange flowers and roses.

2. Heat some concentrated sulphuric acid with a small crystal of potassium dichromate (or ammonium molybdate) and then add a trace of atropine. An aromatic odor is developed, similar to oil of bitter almonds.

VOLUMETRIC ANALYSIS.

INTRODUCTION.

Quantitative determination of the different elements or groups contained in a substance may be accomplished in the **dry way,** by fire tests, and is then called **assaying,** and mostly resorted to for the analysis of ores for metallurgic purposes. Or it may be done in the **wet way,** as in the majority of other cases, and is then conducted according to two principal methods.

In the one, the **gravimetric,** the quantities of the constitnents are determined by separating and converting them into known solid compounds, which are acurately **weighed** and from which the quantities of the elements or groups of the original compounds are calculated.

For example: To determine the amount of silver in lunar caustic, a definite quantity is weighed out, dissolved in water, and hydrochloric acid, or sodium chloride, added in sufficient excess, to convert all the silver present into silver chloride. This being insoluble, is separated by filtration, washed on the filter, dried at 110° C and then placed into a weighed porcelain crucible; the filter is incinerated and the silver chloride heated to beginning fusion, (reduced particles must be redissolved and reconverted into chloride). The cooled crucible is weighed, the weight of crucible and filterash is deducted, and thus the amount of silver chloride is found, and from it, by an easy calculation, the silver. **$AgCl$: Ag**$=143.05:107.68$.

All of the operations must be performed with caution and require considerable time and skill.

In quantitative determinations by the **volumetric** method a different plan is pursued. A weighed quantity of the substance is dissolved and to it a standardized solution of the appropriate reagent is added until a certain reaction is **just completed,** no excess being allowed. The volume of the solution of the reagent expended is **measured** by suitable instruments, and from the quantity of the substance is calculated.

To determine the amount of silver in lunar caustic by **volumetric** analysis, a definite quantity is weighed out and dissolved in water as before, and then a standard solution of sodium chloride is added from a graduated tube, until all the silver is accurately precipitated as silver chloride. The **volume** of the standard solution is noted and from it the quantity of silver calculated, which is necessary to form silver chloride with it. The necessity of filtering, drying, igniting and weighing the precipitate, which would be necessary in the gravimetric method, is thus dispensed with, and the result arrived at in less than one-tenth of the time, and yet with the utmost accuracy.

Not every substance however is suitable for volumetric determination, but a great number may be analyzed by this expeditious method even by persons who can not command the skill and experience requisite for gravimetric analysis. In many manufacturing establishments ordinary workmen are instructed in volumetric methods for determining the strength of products manufactured and use empirical solutions suited to the special requirements and differing in various places. For the general purposes of the analyst the solutions of volumetric reagents have been brought into a uniform system which enables the comparison of results and the interchange of the standard solutions. From the habit of noting on the label the title (french : titre) and strength of the solution of reagents, the name of the method: **titration,** has been derived, which has been used as a synonym for volumetric analysis. We speak of volumetric solutions having a certain **titre**, i.e., adjustment of strength, of a **titrimetric**, i.e., **volumetric** system, etc.

SYSTEM OF STANDARD SOLUTIONS.

The reagents used in volumetric analysis are adjusted according to a uniform system, so that each solution contains within a litre (1000 cubic centimeters) the weight of 1 atom or molecule of the active reagent expressed in grammes. In case of monatomic elements or monobasic acids, or mon-acid bases, this rule applies without exception.

In case diatomic elements or dibasic acids, etc., are used as reagents, only one half of this quantity is used, and generally such part of the weight of the molecule expressed in grammes, is contained in 1 litre of solution, as corresponds to the saturating power of a monatomic element, a mon-acid base, or a monobasic acid.

These solutions are called **normal solutions.** When these would prove too concentrated for some operations, they are made weaker, so as to contain only one tenth of the strength of normal solutions and these dilutions are called: **deci-normal** or **one-tenth normal** solutions. In a few cases even more dilute solutions are used, containing only one onehundredth of the strength of normal solutions. These are designated as **centi-normal** or **onehundredth normal** solutions.

To illustrate by example: The molecular weight of potassium hydrate **KOH**, is 55,98. **Normal** solution of potassium hydrate contains therefor 55,98 grammes of **KOH**, dissolved in enough distilled water to occupy (at the normal temperature, for which the measures are graduated) a volume of 1000 cubic centimeters

Deci-normal solution would contain 5,6 grammes of **KOH** and **centi-normal** 0,56 grammes.

The molecular weight of H_2SO_4 is 97,92, hence the amount of sulphuric acid in one litre of normal solution must be one half that quantity, for H_2SO_4 is dibasic, capable of saturating **2KOH.** Thus **normal** solution of sulphuric acid contains 48,96 grammes in 1000 C.C.: **deci-normal**=4,9 gr. **centi-normal**=0,49 gr.

The corresponding solutions of **KOH** and H_2SO_4 will accurately saturate each other, when equal numbers of C.C. of each are taken. Some volumetric solutions are, for convenience's sake, adjusted to correspond to a certain unit of the specialsubstance, they are to react with, such as Fehling's solution of cupric tartrate or Liebig's solution of mercuric nitrate; these do not belong to the system, but are empirical volumetric solutions. The quantity of the substance to be tested is in case of **empirical** solutions especially determined for each case. In case of **normal** solutions there is to be used one tenth of the atomic or molecular weight of the substance to be tested for, expressed in grammes (if the substance be monatomic or monobasic etc., otherwise reduced to that standard.) For **deci-normal** solution one onehundredth of the atomic weight is taken. This so adjusts the proportion between the substance and the reagent solution, that if the substance be entirely pure, the one tenth atomic weight will react with one tenth litre or 100 C.C. of the solution, which indicate 100 per cent of purity. But if the substance be less pure, then the number of C.C. requisite to complete the reaction will be less than 100 and will directly indicate the percentage of pure substance contained in the sample.

To illustrate by example: Hydrochloric acid, U. S. P., is to be tested by normal solution of potassium hydrate. One molecule of each will be requisite for saturation. We weigh out one tenth of the molecular weight of **HCl** in grammes=3,637 gr. this, if the acid solution consists only of **HCl**, must completely saturate 100 C.C. of **KOH** normal solution. But as it only contains some **HCl**, dissolved in water, it requires only 31,9 C.C. of normal **KOH** solution, hence the hydrochloric acid contains 31,9 per cent of **HCl**, the balance being water; which is the strength prescribed by the pharmacopœia.

Standard solutions for volumetric analysis are often employed in pairs corresponding to each other and each forming the complement of the other, so that whenever a test is either accidently or purposely overdone with one of them, the neutrality will be restored by the other, so that the quantity used of one for neutralization will exactly equal the quantity used in excess of the other. Thus we have the following pairs:

Potassium hydrate and **sulphuric acid.**
Potassium permanganate and **oxalic acid.**
Iodine and **sodium hyposulphite.**
Silver nitrate and **sodium chloride**, etc., etc.

Some volumetric solutions, remain for an indefinite time unaffected by atmospheric or other influences, and when once accurately adjusted are reliable for years, especially if preserved in small glass stoppered bottles, sealed with paraffin and kept protected from light and excessive changes of temperature. Others change rapidly, even with greatest care, and must be either frequently renewed, or their standard must be readjusted by adding enough of a more concentrated solution, to compensate the loss. This is called **placing** or **adjusting** the **titre,** or else the **titre** is **taken,** i.e., the strength is ascertained and its difference from the standard corrected in the calculation subsequently.

VARIOUS METHODS OF DETERMINATION.

Volumetric analysis may either be effected by **direct** or by **indirect** determination or by the method of **residues** (rest-analysis.)

a. **Direct method.** By this we determine the quantity of an acid directly by neutralization with normal alkali solution; or the quantity of iodine by adding a solution of sodium hyposulphite, until the color of iodide of starch disappears; or in general terms by determining the quantity of the unknown body by direct measurement of the quantity of the reagents added to it until either the saturation or other effect is completed. This is a most accurate method, but only applicable to soluble substances.

b. **Indirect method.** Many insoluble substances cannot be directly determined. Some, as certain peroxides and oxygen-acids ($\mathbf{MnO_2}$. $\mathbf{PbO_2}$. $\mathbf{BaO_2}$, $\mathbf{CrO_3}$, $\mathbf{HClO_3}$, etc., furnish, when boiled with strong **HCl** a definite amount of free **chlorine.** Now as **iodine** may be determined more accurately than **chlorine,** it is best to let **Cl** be absorbed by **KI,** liberating an equivalent amount of **I** to be measured by standard solution of sodium hyposulphite. Even in such indirect measurements the quantity of the reagent used is in direct proportion to the quantity of the substance tested; hence some authors unite both methods under the title of direct. In the following method the process is reversed.

c. **Method of residues.** In this process the substance is incapable of being determined directly, but other substances capable of volumetric determination are made to react upon it and an accurate measure of them is added in excess of the required quantity. A part is then so modified or destroyed, that it will no longer react with the standard solution, so that we can only measure the **residue**, the rest in excess of the requirement, and from this calculate the quantity used up and the equivalent proportion of the original substance.

To illustrate by an example: Calcium carbonate cannot well be directly determined. An accurately measured quantity of nitric acid, or hydrochloric acid, of known strength, more than sufficient to decompose the calcium carbonate is used and after the reaction is complete, standard solution of **KOH** is used to measure the **rest** or **residue** of free acid.

INDICATORS.

The completion of the reaction must be closely observed, so as to know the accurate measure of the reagent necessary for saturation or other chemical change produced. In many cases this final point is indicated by a **change of color** of the solution, in others by the **formation** or cessation of a **precipitate**. In other cases it is either difficult or impossible to determine accurately the end of the reaction between the substance tested and the volumetric reagent, unless other substances are used to indicate with precision this final point. Such substances are called **indicators** and are either mixed with the substance to be analyzed at once, or else employed by the **method of spotting** (Tüpfel methode) which consists in taking a drop from the solution and adding it to the indicator, either on a white porcelain plate, or on filter paper, so that a change of color may reveal the state of saturation of the solution treated with the volumetric standard.

Starchpaste is used as indicator for **iodine.**

Potassium dichromate and **potassium sulpho-cyanide** are indicators for **silver.**

Phenolphtaleine or **litmus** solutions are the principal indicators for **alkalies** and **acids.**

Alkaline lead solution, **ferro-cyanide** and **ferri-cyanide** of **potassium** are among the indicators used in **spotting.**

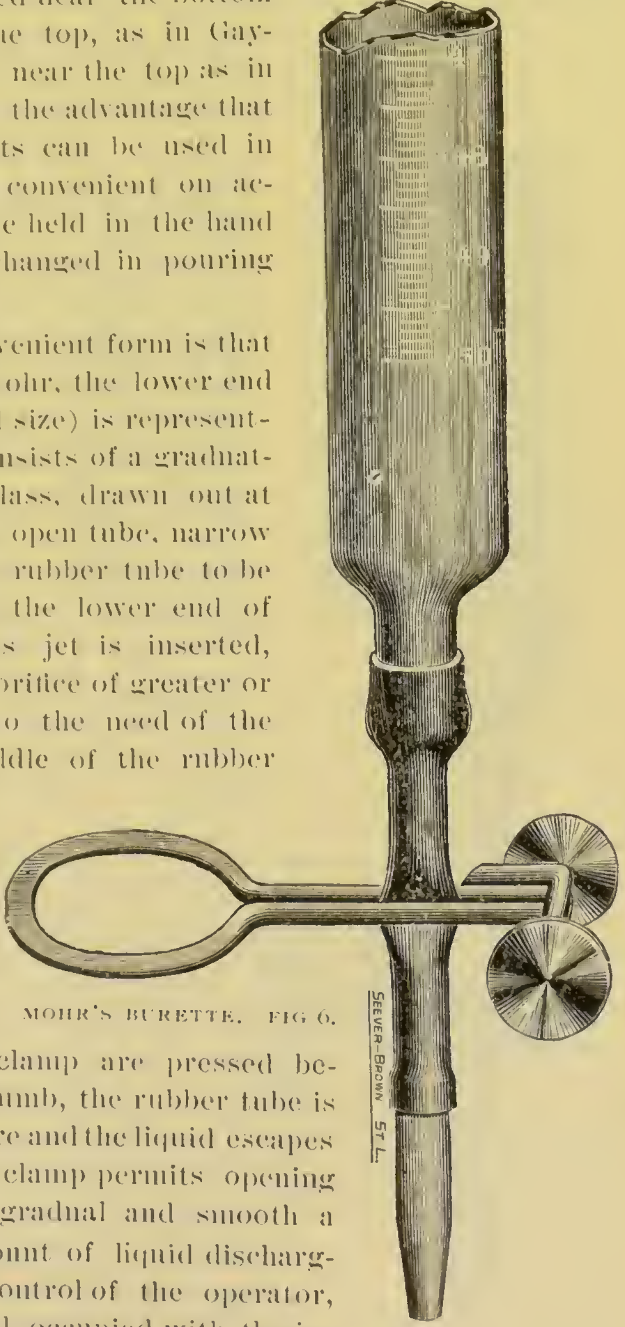
VOLUMETRIC INSTRUMENTS.

The most important instruments for volumetric determinations are: the **burette,** the **pipette,** and the **measuring flask.** Of these, various forms are used, suitable for different operations. Besides these a variety of other apparatus, not specifically volumetric is necessary, such as glass flasks, beakerglasses, porcelain dishes, funnels, etc., which do not differ from those employed for the purposes of qualitative analysis. A great number of special instruments have been devised, to facilitate certain processes, but most of these may be dispensed with in ordinary work.

a. Burettes.

A burette is a glass tube, graduated generally into cubic centimeters and their subdivisions, from which the volumetric test-solutions are to be delivered into the substance to be examined. The older forms were closed at the bottom and provided with a spout, either attached near the bottom and extending to the top, as in Gay-Lussac's burette or near the top as in Bink's. These have the advantage that all kinds of reagents can be used in them, but are less convenient on account of having to be held in the hand and their position changed in pouring out.

A much more convenient form is that devised by Dr. F. Mohr, the lower end of which (in natural size) is represented in fig 6. This consists of a graduated tube of heavy glass, drawn out at the lower end to an open tube, narrow enough to permit a rubber tube to be secured to it, into the lower end of which a small glass jet is inserted, whose point has an orifice of greater or less size according to the need of the operator. The middle of the rubber tube, between the graduated tube and the jet, is compressed by means of a **spring-clamp**, to prevent the escape of liquid. When the two buttons of the clamp are pressed between finger and thumb, the rubber tube is relieved from pressure and the liquid escapes from the jet. The clamp permits opening and shutting in so gradual and smooth a manner, that the amount of liquid discharged is under perfect control of the operator, who has but one hand occupied with the instrument, while the other is entirely free



MOHR'S BURETTE. FIG 6.

to hold or shake the flask or beaker into which the test liquid is delivered. This advantage is so great that Mohr's burette is preferred for all operations in which the test liquid does not corrode the rubber and is thereby decomposed. It is fastened to a holder, which clamps it securely and permits its adjustment to flasks and beakers of various heights. Whenever iodine, or silver nitrate or potassium permaganate are to be used, no burette can be employed in which the liquid comes in contact with rubber. For these solutions another burette must be used, and the most eligible is Geissler's form with straight glass stopcock, the lower end of which is represented, in natural size, in fig. 7. The glass stopcock does not afford the delicacy of touch, which characterizes the spring-clamp; to insure close fitting and accurate adjustment, it requires the use of both hands, the left supporting the opposite side of the stop cock, while the right turns the handle, yet it is far superior to any of the instruments requiring pouring. As it is suitable for all liquids, those who wish to own but a single burette for all operations, will do well to select this form.

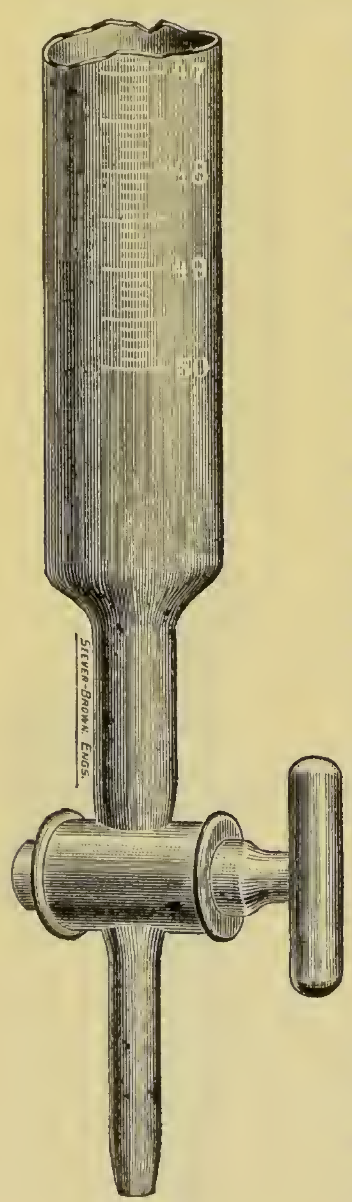


FIG. 7.

Burettes are filled with the volumetric solutions by means of small funnels, care being taken to avoid foaming; the stop cock is closed and the liquid is poured in so as to stand considerably above the zero of the gradation. The stop cock is rapidly opened, and shut again as soon as the jet below it is entirely filled, no air bubble being allowed to remain. The solution is then adjusted to the zero point.

As the liquid in the glass tube will not stand on a level, but rise on its edges, and leave a depression in the centre, it is necessary to observe carefully the appearances of the upper surface of the liquid, so as to secure uniform reading of the graduations.

The following figures, 8, 9 and 10, show these appearances in transparent liquids.

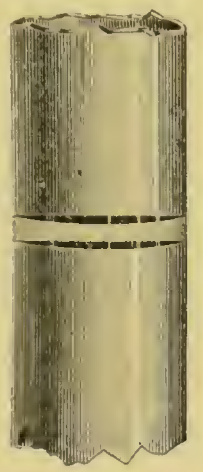


FIG. 8.

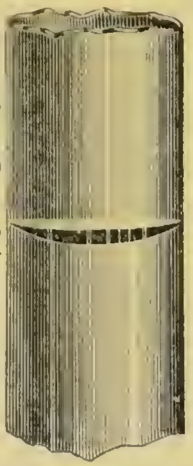


FIG. 9.

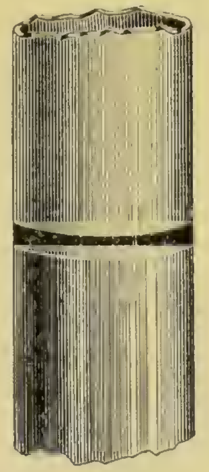


FIG. 10.

When the liquid is viewed against a dark background two dark menisci appear, separated by a lighter interval, fig. 8. With a light background, such as a white wall, or a window, a white meniscus shows above a dark one, and the surface appears like fig. 9. When a piece of white paper is held closely behind the tube, so as to reflect the light coming from the rear of the observer, there are two white curves, separated by a dark space. In whatever position the burette is placed, the reading for transparent liquids is done from the lowest margin of the curve. Opaque liquids do not show these reflections and the graduation is read from the upper margin.

When burettes are not entirely clean, or when their contents are to be changed, they must be thoroughly rinsed with water, then with distilled water, and finally with some of the test solution, which they are to contain.

b. Pipettes.

Pipettes are glass tubes having a narrow stem, a larger cylindrical or globular body and a tapering, narrow point. They are either provided with a mark on the narrow stem, indicating the limit of their capacity (which is marked on the body) or graduated on their cylindric body into cubic centimeters and their subdivisions. Sometimes both mark and graduation are united in one instrument, as shown in fig. 11. which shows a pipette graduated for 5 C.C. into $^1/_{10}$ C.C. and with mark on neck for 10 C.C. The mark on neck should be as near the body as possible. Pipettes vary in capacity from 1 C.C. to 100 C.C. and more. Those like fig. 11. are most useful for general purposes, but it is best to have an assortment.

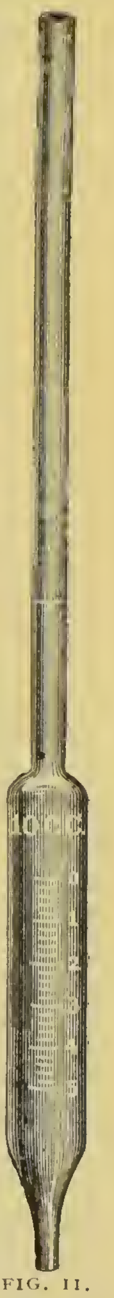


FIG. 11.

A pipette is filled by holding it between thumb and middle finger, the point dipping into the liquid, the mouth sucking at the upper orifice until the liquid stands above the mark. The index finger is then quickly pressed upon the orifice of the stem, and by a gentle release of pressure the liquid is permitted to flow out until it stands so that the lower margin of the liquid curve coincides with the mark or graduation. The drop adhering to the point is struck off.

It is emptied by holding it over the receiving vessel and releasing the pressure of the finger until the desired point of the graduation has been reached (when the finger must again firmly close the upper orifice) or until it has been emptied. In either case the drop adhering to the end belongs to the liquid delivered, and is struck off against the wall of the receiving vessel, so as to unite with the contents.

c. Measuring Flasks.

Measuring flasks are also of two kinds. The one has a globular body with narrow neck, on which a mark is engraved, indicating the limit of the liquid the flask is gauged to contain. The capacity is generally 1 litre, ½ L. ¼ L. ⅛ L. and $^1/_{10}$ L; though other sizes are occasionally used. They are employed for making standard solutions; the quantity of dry salt weighed out for a litre it is placed into the litre flask, some of the solvent is added and they are shaken together, until dissolved; then the flask is filled up to the mark and the liquid well mixed by shaking.

When a deci-normal solution is to be made, the 1/10 litre flask is filled to the mark with the normal solution; this is transferred to the litre flask, which is filled to the mark with the solvent and well mixed.

These flasks are also useful for accurate dilutions of substances to be tested. If, e. g. there is a small quantity of substance to be divided into ten equal parts, the substance is dissolved into the 1/10 L. flask, (100 C.C.) which is filled to the mark. By means of the 10 C.C. pipette exactly one tenth can now be measured out.

All flasks are gauged to **contain** the quantity marked on them, while pipettes are gauged to **deliver** the quantity marked, allowance being made for the liquid adhering to their inner surface after the drop has been struck off from the point. In gauging flasks, the quantity of distilled water, corresponding to their capacity, is weighed into them at the normal temperature of 17.5°C. Hence no allowance is made for liquid adhering to their sides. A 1 L. flask holds 1 kilogramme of water at 17.5°C; a 100 C.C. flask holds 100 grammes of water. Another kind of measuring flask is cylindrical, and graduated throughout its body into C.C. or their multiples. They are of great assistance in adjusting the titre of standard solutions.

CLASSIFICATION OF VOLUMETRIC PROCESSES.

Volumetric analysis includes several processes, based upon the occurrence of saturation, oxidation and reduction, and precipitation.

a. **Saturation,** underlies all the processes of **acidimetry** and **alkalimetry** and requires standard solutions of **alkalies** and of **acids,** together with indicators, for which a solution of phenolphthaleine is now preferred to the litmus formerly used.

b. **Oxidation** and **reduction,** takes place between **potassium permanganate** (chameleon) as oxidizer and **oxalic acid** or ferrous salts, as reducents. Or **potassium dichromate** is employed as the oxidizer, **ferrous salts** being the reducents to be tested. A similar antagonistic action between **iodine** and **sodium hyposulphite** or **sodium arsenite,** renders them applicable to a great number of determinations, especially by the indirect method.

c. **Precipitation.** In the many processes in which a precipitate is formed by the reagent with the solution of the substance under examination, the first formation of a precipitate or the cessation of precipitation is observed as the final point of the reaction. Indicators must often be employed to render the end of the reaction clearly perceptible. There are to be noted among the test solutions in the titrimetric system:

Silver nitrate and **sodium chloride,** used as correlatives.

Mercuric chloride and **sodium chloride.**

Also the empirical solutions of **mercuric nitrate,** as test for **urea,** and **cupric tartrate** (Fehling's solution) for **glucose.**

Many others are used for special processes.

In the succeeding pages the preparation and use of the test solutions will be described and some examples of each method given.

ACIDIMETRY AND ALKALIMETRY.

OXALIC ACID.

Crystallized oxalic acid has the constitution $H_2C_2O_4+2H_2O$. It is not readily changed in this composition by atmospheric influences and may easily be obtained quite pure. It is therefore very suitable to form the basis of the series of test solutions used for determination of alkalies and acids. Its molecular weight is 126. Being dibasic, i. e., capable of combining with two atoms of **K** or **Na**, one half of its weight is taken for the normal solution.

Weigh 63 grammes of crystallized oxalic acid, put them into a 1 litre flask and fill it about half to two thirds full of distilled water. Shake the mixture until all the acid is dissolved and then add enough distilled water to fill to the mark and mix thoroughly. The temperature should be 17.5°C. This forms the **normal** solution.

To make **deci-normal**, which is often employed against decinormal potassium permanganate, fill a 100 C.C. flask with normal solution, pour it carefully into the litre flask, and finally fill this up to the mark, and mix thoroughly.

The strength of the solutions should be marked on the label as well as the name.

In this as well as some of the other standard solutions, the weights have been given to correspond with those of the U. S. Pharmacopoeia, and other manuals, instead of those deduced from the latest corrections of the atomic weights, as given on page 1. Thus the molecular weight of oxalic acid, as corrected, is really 125.7 instead of 126, hence one-half should be 62.85 instead of 63. Sulphuric acid has a molecular weight of 97.82 instead of 98, and one-half of this should be 48.91 instead of 49. But in ordinary practice the difference amounts to so little, that the decimals may safely be rounded off, more especially, as the titre is adjusted by comparison of the standard solutions with each other, and the error falls within very narrow limits.

SULPHURIC ACID.

This is preferred by many for alkalimetric operations because it does not evaporate so readily, nor leaves any solid residue in the jets when evaporated, as oxalic acid does. It will bear boiling without loss, which cannot be said of hydrochloric or nitric acid solutions. Pure concentrated sulphuric acid is easily enough obtainable, but on account of attracting water from the atmosphere, changes its hydration so quickly, that normal solution cannot be made directly. In an acid diluted approximately to the standard the sulphuric acid may be determined gravimetrically, and the titre then adjusted, or else it may be brought to the standard strength by titration with normal alkali. In whatever way obtained, it will contain 49 grammes of $\mathbf{H_2SO_4}$ in 1000 C.C. of solution and may then be used instead of oxalic acid volume for volume.

HYDROCHLORIC ACID.

Normal solution of hydrochloric acid is for some purposes preferable to either sulphuric or oxalic, as it forms soluble salts with alkaline earths. It is made by diluting pure concentrated **HCl** and adjusting the titre either against normal silver nitrate solution or against normal alkali solution. It contains in the **normal** solution 36.5 grammes of **HCl** in one litre, and is equivalent to normal oxalic and sulphuric acid volume for volume.

POTASSIUM HYDRATE.

Pure solid potassium hydrate is difficult to obtain and hard to preserve in purity on account of being changed by atmospheric influences. Hence it is not suitable for weighing and dissolving so as to make a standard solution. The molecular weight of **KOH** is 55.98 (usually taken as 56 in volumetric solution.) But if 56 grammes of even the purest article in the market are taken, it will not contain nearly so much of real **KOH**, moisture attracted from the atmosphere adding more or less weight. Hence a sufficiently large amount is taken say 59 to 60 grammes and dissolved in a litre of water. Ten cubic centimeters of the solution are then put into a small flask and about 2 to 4 drops of phenol-phthaleine solution added which gives it an intense red color. The flask is then placed under the jet of a burette filled with **normal oxalic acid** solution and the acid allowed to flow slowly into the flask containing the red colored alkali solution, from time to time the flask is shaken, to mix its contents thoroughly. At last a single drop of the acid will discharge the red color. If reading the scale of the burette indicates that exactly 10 C. C. of acid have been used to neutralize and decolorize the alkaline solution, then it is very nearly normal and the test must be repeated with a larger quantity. If more then 10 C. C. acid was used, then the alkali solution is too strong and must be proportionately diluted. Supposing that 11 C. C. acid were used. We have 990 C. C. potassium solution remaining of the 1 litre and these have a strength of 11 instead of 10 hence we count 10 : 11=990 :x. This gives the result as 1089 and this is the number of cubic centimeters to which the solution must be diluted to correspond in strength to normal acid. 99 C. C. must therefore be added to the 990 remaining of the litre after taking out the 10 C. C. for trial. The solution must be again tested as before, until it is absolutely equivalent to the acid. In the final test 50 C. C. of potassium solution are taken, 8 or 10 drops of phenol-phthaleine are added to render its color deep red. When the 50 C. C. of acid are added, the color must disappear with the last drop, and reappear if one drop of potassium hydrate is added. Normal solution of potassium hydrate must be kept in small bottles with well paraffined glass stoppers. It is preferable to sodium hydrate in attacking glass less and giving less foam in filling the burettes. In regard to absorption of carbonic acid gas from the atmosphere, there is little difference between the two in this state of dilution.

SODIUM HYDRATE.

Normal solution of sodium hydrate is adopted by the U. S. Pharmacopoeia, **$NaOH=40$.** It is made in the same manner as potassium hydrate and can be used instead of it volume for volume. On account of its foaming and corroding glass more rapidly, it is hardly as eligible as potassium hydrate. The same indicator is used as with potassium.

SODIUM CARBONATE.

Sodium carbonate, **$Na_2CO_3+10H_2O$,** is obtainable in great purity, though of very inconstant amount of water. It must be made anhydrous by heating the air-dry powder and weighed as soon as cool. 53 grammes of anhydrous are required for 1 litre of normal solution. The somewhat troublesome interference of the carbonic acid with observing the final point has led to its abandonment by most analysts. Nevertheless it is valuable as giving, like oxalic acid, a starting point for the accurate adjustment of the whole series of normal solutions of acids and alkalies. The mode of managing the titration of a carbonate will be shown below among the examples for practice.

AMMONIUM HYDRATE.

Ammonium hydrate, **NH_4OH,** gives off vapors of **NH_3** very readily and concentrated solutions are therefore very liable to change in strength. It also acts on glass more than potassium hydrate of equivalent concentration. It cannot therefore be advantageously employed in **normal** strength but is made **half-normal,** so that 2 C. C. correspond to 1 C. C. of acid. This solution is made by the same method as potassium hydrate, taking phenol-phthaleine as indicator. **Half-normal** solution contains 17.5 grammes of **NH_4OH** (=8.5 grammes of **NH_3**) in one litre. It is preserved and used just as potassium hydrate.

BARIUM HYDRATE.

$Ba(OH)_2$ has a molecular weight of 170.68; being a **di-acid** base, one half of this=85.34 grammes would be contained in 1 litre of normal solution. But in that strength it would not be soluble in cold water, hence **half-normal** or **deci-normal** solution must be used. As it rapidly absorbs **CO_2** from the air, it must be preserved and handled with special precaution. The pure crystals contain **$Ba(OH)_2+8H_2O$.** The water in which they are dissolved must be previously boiled to expel **CO_2.** As indicator, heretofore, turmeric paper has been employed, by the method of spotting, but phenol-phthaleine added directly to the solution gives very satisfactory results, even when used against sulphuric acid; the white precipitate of barium sulphate does not interfere with a sharp indication of the final point.

SATURATION EQUIVALENTS.

The saturation equivalents of the foregoing normal solutions are stated below, so that the number of grammes of substance required to saturate 100 C. C. of either of the normal acid or alkali solutions are given. If this quantity of the substance, to be tested, is taken, then each 1 C. C. of normal solution used for saturation indicates 1 per cent of pure substance contained in the specimen tested.

A. NORMAL ACID SOLUTION.

100 C.C. correspond to:	Grammes.
NH_3	1.700
NH_4OH	3.500
$NH_4HCO_3.NH_4NH_2CO_2$	5.233
KOH	5.600
K_2CO_3	6.900
$KHCO_3$	10.000
$NaOH$	4.000
Na_2CO_3	5.300
$Na_2CO_3+10H_2O$	14.300
$NaHCO_3$	8.400
$Ca\ (OH)_2$	3.700
$CaCO_3$	5.000
$Ba(OH)_2$	8.534

B. NORMAL ALKALI SOLUTION.

100 C.C. correspond to:	Grammes.
H_2SO_4	4.900
HNO_3	6.300
HCl	3.640
HI	12.760
HBr	8.080

$HCHO_2$ (formic)	4.600
$HC_2H_3O_2$ (acetic)	6.000
$H_2C_2O_4+2H_2O$ (oxalic)	6.300
$H_2C_4H_4O_6$ (tartaric)	7.500
$H_3C_6H_5O_7+H_2O$ (citric)	7.000
$HC_3H_5O_3$ (lactic)	9.000
$H.C_7H_5O_3$ (salicylic)	13.800
$H.C_7H_5O_2$ (benzoic)	12.200

CHOICE OF INDICATOR.

As the point of saturation of acid by alkali is not recognizable by observation of the resulting solution, indicators must be used, to show with accuracy the end of the reaction. For this purpose litmus solution has been long in use. It gives two color reactions. With acid it turns red, with alkalies blue. Alkaline dicarbonates give an intermediate violet tint. Recently phenol-phthaleine, **$C_6H_4(CO)_2(C_6H_4.OH)_2$**, is preferred, which is dissolved in about 100 parts of dilute alcohol and added in small quantities to the liquid to be tested. With alkaline hydrates and neutral carbonates it gives an intense blood red color; with neutral salts, or acids it appears colorless. Hence the first drop of excess of alkali added to a solution, containing the indicator, will show itself by the red color, while, as soon as neutrality is reached, the color disappears. In the case of carbonates phenol-phthaleine behaves as follows. So long as a neutral carbonate is present, the liquid remains red, as soon as only bicarbonate remains, the color disappears. A number of other color indicators have been proposed, methyl orange, cochineal, logwood, etc., but none have proven as satisfactory as phenol-phthaleine.

Example 1. Aqua Ammoniae.

According to U. S. P. this contains 10 per cent by weight of **NH_3** gas. Its specific gravity is 0.959 at 15°C; 8.5 grammes, measuring 8.9 C. C. should neutralize 50 C. C. normal acid solution.

1000 C. C. normal acid correspond to 17 grammes **NH_3**. A 10 per cent solution contains only one tenth as much and hence 100 C. C. acid are required to neutralize 17 grammes of aqua ammoniae containing 10 per cent **NH_3**. To operate conveniently with the **measuring** instrument, the 17 grammes by weight are according to the specific gravity reduced to measure as follows: 0.959gr.: 1.0 C. C. = 17gr.: x C. C. resulting in 17.72 C. C. of acid. Half of these figures gives the quantities directed by the pharmacopœia.

Fill the burette graduated for 50 C. C. into one tenths with normal sulphuric or oxalic or hydrochloric acid. See that the jet is full and free from air bubbles. Adjust to the zero mark of the scale.

Into a flask of about 200 C. C. capacity measure 8.9 C. C. Aqua ammoniae, add 4 drops of solution of phenol-phthaleine, which will give an intense red color to the solution. Place under the jet of the burette, which must be so raised or lowered in its holder, that the jet is slightly projecting into the neck of the flask, so that no drop can fall outside, yet that the flask can be easily removed from under it. Now open the spring-clamp or stopcock, so as to let the acid flow slowly into the flask. From time to time shut off the flow and shake the flask sufficiently to mix the contents well. As soon as the point of saturation is neared, single drops only are permitted to fall into the flask and agitation takes place after every drop. At last the color will suddenly disappear by the addition of a single drop.

The graduation is now read off, and if exactly 50 C. C., the ammonia water is of officinal strength. If more is required, the burette (which is assumed to be graduated for 50 C. C.) must be refilled and the operation continued with the new supply.

Supposing that 60 C. C. of normal acid have been needed instead of 50 C. C., then the ammonia water contains 12 per cent of **NH_3** instead of 10 as required. 50 C. C. : 60 C. C. =10 0/0: 12 0/0. If a less number, say 40 C. C. of acid were needed, the preparation is too weak. 50 C. C.: 40 C. C.=10 per cent.: 8 per cent. If no graduated pipette is at hand with which to measure the fractional C. C. of the substance but only a pipette holding 10 C. C. it is easily to calculate the number of C. C. of normal acid necessary to saturate exactly 10 C. C. of the liquid, according to the following consideration: if 17.72 C. C. require 100, how many are required for 10? 17.72 ammonia: 100 acid = 10 ammonia: 56.4 acid. So the 10 C. C. pipette can be substituted for a graduated one, by calculating, as above, in any case where fractions cannot be conveniently measured by the graduated pipette.

Example 2. Sodium Carbonate.

This salt crystallizes with 10 molecules of water, but effloresces in dry air, parting with various quantities of water. Hence its value is quite uncertain and requires to be determined by analysis. The U. S. P. allows for 2 per cent of impurities of the crystals with full amount of water of crystallization, but as the air-dry salt is often used, it is best to determine its real contents of anhydrous sodium carbonate. $\mathbf{Na_2CO_3 + 10H_2O}$ has a molecular weight of 286. $\mathbf{Na_2CO_3 = 106}$. As in this salt there are 2 atoms of **Na**, 53 grammes will be required to saturate 1 litre of normal acid, or 5.3 to saturate 100 C. C. Hence we weigh out 5.3 grammes of the salt. If it were pure **anyhdrous** $\mathbf{Na_2CO_3}$, t would require 100 C. C. of acid, each 1 C. C. indicating 1 per cent. But if the salt contains half water, 50 C. C. of acid will only be needed, corresponding to 50 per cent. If it is pure crystallized salt of 10 molecules of water, it will require only 37.06 C. C. of acid, corresponding to 37.06 per cent of anhydrous sodium carbonate.

To make the analysis, fill the burette as before (example 1) with normal sulphuric (or oxalic, or hydrochloric) acid. Weigh 5.3 grammes of the salt and dissolve them in a flask (holding about 200 C. C.) in about 20 to 30 C. C. of water. Add 4 to 6 drops of phenol-phthaleine solution, which produces a deep red color. Let the acid flow into the flask, in a moderate stream, until the liquid becomes colorless. This, in the case of a carbonate, does not as yet show saturation, but that enough $\mathbf{CO_2}$ has been liberated in the solution to convert the residue of neutral sodium carbonate, $\mathbf{Na_2CO_3}$, into sodium dicarbonate, $\mathbf{NaHCO_3}$, which does not color the phenol-phthaleine. The flask is now removed from the burette and heated over a lamp, to boil out the $\mathbf{CO_2}$, which readily parts from the dicarbonate at boiling heat. The solution will again become red. It is again placed under the burette and acid is carefully added till the red color is again discharged. It is boiled again and the process repeated till the boiling fails to restore the color. A few light splinters of glass-tubing thrown into the flask will accelerate the boiling considerably. The graduation is now read off and

and from it the percentage of Na_2CO_3 is calculated. If e.g. there were used 36.3 C. C. of normal acid, the specimen contains 36.3 per cent of anhydrous or 98 per cent of crystallized soda, the standard used by the U. S. P. For absolutely pure crystallized salt requires, as above stated, 37.06 C. C. of acid, this would correspond to 37.06 per cent of anhydrous or 100 per of crystallized salt.

37.06 C. C.: 36.3 C. C.=100 per cent: 98 per cent.

Example 3. Acetic Acid.

Acetic acid of U. S. P. contains 36 per cent of $H.C_2H_3O_2$ and 64 per cent of water, and 6.0 grammes should require 36 C. C. of normal alkali solution. The specific gravity of acetic acid is 1.058 at 15^0 C. The molecular weight of the absolute acid is 60; being monobasic 6 grammes of pure absolute acid accurately neutralize 100 C. C. of normal solution of potassium hydrate and if 6 grammes are weighed out, every 1 C. C. of alkali used indicates 1 per cent of real acetic acid in the mixture of acid and water. If the acid is not too far from the U. S. P. standard, so as to vary the specific gravity materially, instead of 6 grammes there may be taken 5.72 C. C. Or else to simplify measuring there may be taken 10 C. C. which should then require 63.9 C. C. of normal alkali solution to reach the standard of 36 per cent.

Fill the well-cleaned burette with normal solution of potassium hydrate. Adjust jet and zero mark. Measure into a flask containing about 200 C. C., as used in foregoing examples, 5.72 C. C. of acetic acid, U. S. P. add four drops of phenolphthaleine solution and let the normal potassium solution flow slowly into the flask. Wherever a drop falls, a red color is produced which quickly disappears again, until the saturation point is approached. Then after every addition of a drop of alkali the flask is shaken to mix the contents thoroughly. Finally a single drop in excess of saturation will produce a permanent red color. The burette is read off, about one twentieth of 1 C. C. is deducted from the number for the drop in excess, the remainder gives directly the percentage of real acetic acid.

As pipettes or burettes are only graduated into tenths of cubic centimeters the fractions of these must be estimated, or else measured as follows: to measure 5.72 C. C. of acetic acid, put 10 C. C. of the acid into a 100 C. C. flask and fill up to mark with distilled water. Of these 100 C. C. 57.2 are now measured out, which contain accurately 5.72 C. C. of undiluted acid.

Example 4. White Wine.

Wine contains tartaric acid either free or as tartrates, besides this occasionally, other organic acids are present. In estimating the total amount of acids in wine their measure is generally expressed in terms of tartaric acid. The U. S. P. places the limits of acidity so, that 250 C. C. of wine should require, for complete neutralization, not less than 15 C. C., nor more than 26 C. C. of normal alkali solution. This is equal to 0.45 per cent as minimum and 0.78 per cent as maximum of acid allowed. (Many very excellent native wines exceed this limit, apparently without prejudice to their popularity.)

When the absolute percentage of acid, expressed in terms of tartaric acid, is to be determined, the following course is adopted.

Tartaric acid, $H_2.C_4H_4O_6$, has a molecular weight of 150; as it is di-basic, 75 grammes will neutralize 1 litre of normal potassium hydrate, or normal sodium, or ammonium hydrate. Hence 7.5 grammes = 100 C. C. The number of grammes may be converted into C. C. by calculating the specific gravity, which range from 0.990 to 1.010 and frequently differs so little from that of water, that it may be neglected.

Take 7.5 grammes (or its equivalent in C. C.) of wine. If this were pure tartaric acid, 100 C. C. of the alkali would be necessary for solution: 1 C. C. represents 1 per cent of pure tartaric acid. If 0.45 C. C. of normal solution are used, the wine contains 0.45 per cent, the minimum limit of the U. S. P.

For accurate determinations the use of deci-normal solution is to be preferred.

Red wine must be decolorized either by filtration through animal charcoal or by adding to it 10 C. C. deci-normal sulphuric acid and then 10 C. C. deci-normal baryta-water. The precipitated barium sulphate carries with it sufficient of coloring matter, to make visible the change of color in the indicator.

Example 5. Chloral Hydrate.

The molecular weight of chloral hydrate, $C_2HCl_3O + H_2O$ is 165.2. Alkaline hydrates, lime-water and baryta-water decompose it into chloroform and a formate. This reaction occurs in strictly equivalent proportion to the alkali used, when the temperature is kept cool. Baryta-water is preferable as it is less liable to decompose the chloroform than **KOH.** Each 1 C.C. of deci-normal solution of barium hydrate corresponds to the decomposition of 0.01652 grammes of chloral hydrate. The estimation is not made by the direct method, but by the method of residue. A measured quantity of barium hydrate solution is added in excess of the needed quantity to decompose the chloral hydrate. A portion of this is neutralized by the formic acid, and the residue is measured back again by titration with acid.

Weigh 1 gramme chloral hydrate and dissolve in 10 C. C. water; add 70 C. C. deci-normal solution of barium hydrate, and 8 drops of phenol-phthaleine solution. Shake the mixture frequently and after half an hour, or longer time, add, from a burette, enough deci-normal acid solution (best hydrochloric, although sulphuric can be used), until the red color disappears. Supposing 9.5 cubic centimeters were used. They indicate the residue of unchanged baryta-water, and must be deducted from the total quantity added. As 70 C. C. were added at first, 70 C. C. — 9.5 C. C. = 60. 5 C. C. of baryta-water were really necessary to decompose the chloral hydrate. Each 1 C. C. baryta-water = 0.01652 grammes chloral hydrate, hence there were contained in the 1 gramme of the specimen: 60.5 x 0.01652 or 0.99946 grammes of real chloral hydrate, a quantity which differs so little from 1 gramme, the amount employed, that the difference falls within the limits of of errors of observation. The chloral hydrate was pure. To insure accurate results, the chloral hydrate used must be first tested for acidity and if not neutral, must be neutralized with a drop or two of baryta-water.

OXIDIMETRY.

POTASSIUM PERMANGANATE.

Potassium permanganate, $\mathbf{KMnO_4}$, crystallizes without water. Its molecular weight is 156.77. Its application in volumetric analysis depends upon its property of giving off a part of its oxygen to oxidize other compounds, especially oxalic acid to carbonic acid and ferrous salts to ferric. Compare page 31, example XX. 5 and 6. This oxidation requires the presence of enough sulphuric acid to convert the **K** and **Mn** into sulphates.

$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$. In this reaction the two molecules of $KMnO_4$ give off $5\ O$ to convert $5\ H_2C_2O_4$ into $10CO_2 + 5H_2O$. $2KMnO_4 + 10Fe''SO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2'''(SO_4)_3 + 8H_2O$.

In this reaction the two molecules of $KMnO_4$ give off $5\ O$ to convert $10Fe''SO_4 + 5H_2SO_4$ into $5\ Fe_2'''(SO_4)_3$ by removing from $5\ H_2SO_4$ the $5H_2$ to form $5\ H_2O$.

These reactions show, that $5O$ of the $2\ KMnO_4$ are used in oxidizing the **5** molecules of oxalic acid into CO_2 and the rest to liberate the $3\ SO_4$ from their hydrogen, so as they can combine with K_2 and Mn_2. Similarly $5\ O$ are used for the conversion of ferrous into ferric salt, the other $3\ O$ for decomposing the $3\ H_2SO_4$. It follows then that two fifths of the molecular weight of $KMnO_4$, 156.77 or 62.71 grammes are the equivalent of 1 oxygen. But as oxygen is di-atomic and the volumetric normal is calculated for mon-atomic values, this number must be divided by **2** and 31.354 is the number of grammes of pure potassium permanganate required for 1 litre **normal** solution. For most purposes this is too concentrated and **deci-normal** solution, containing 3.135 grammes to the litre is the strength generally employed, while occasionally **centi-normal** solution is used. Not every reaction, in which potassium permanganate acts as oxidizer, takes place so that $5\ O$ of $2\ KMnO_4$ serve to oxidize the substance, like **Fe** or oxalic acid. Cobalt e. g. appropriates but $3\ O$, and therefore requires a different strength of solution, or a correction by calculation. As potassium permanganate is more frequently employed for determination of iron, than any other operation, an **empirical** solution, containing 5.646 grammes of $K\ MnO_4$ in 1 litre, corresponding to **10** grammes of **Fe** and a **deci-empirical**, containing 0.565 grammes in 1 litre have recently been much used. The U. S. P. directs an empirical solution containing 1 gramme in 1000 C. C., but requires that 62.8 C. C. of it should be taken to be the equivalent of 2 C. C. normal oxalic acid, so that the proportion of 31.4 : 1 is also used nearly as in the regular system.

Many analyses formerly made with potassium permanganate have been transferred to other reagents on account of the instability of the permanganate solution as ordinarily made. This required "taking the titre" before every day's work and occasioned no little delay. But when properly made permanganate solution is quite permanent and remains of the same strength for months, if carefully protected from dust. To make it stable requires that two solutions be made of $KMnO_4$ in water, one too concentrated and the other too dilute for the standard, and that both be boiled and set aside, to let precipitates settle for about two days. From these two a mixture is adjusted to the accurate standard by oxalic acid, or by iron, and such mixture retains its titre for many months. Potassium permanganate is best preserved in small glass stoppered flasks, to which a cork with two perforations is fitted, which transmits two bent glass tubes similar in arrangement to the spritz-flask. When the burette is to be filled from the bottle, the glass stopper is temporarily exchanged for the cork and tubes, and the liquid blown into the burette, instead of pouring it out in the ordinary way. Care must be taken that the bottle be not shaken so as to let the liquid come in contact with the cork. Burettes with rubber tube and spring-clamp cannot be used, for contact with any organic substance will decompose the permanganate. Hence a burette with a glass stopcock is chosen.

The final point is determined by the rose red color of the solution, produced by a single drop of permanganate in excess, remaining for some time. The excess used must be deducted from the total read off on the graduation of the burette.

Example 6. Oxalic Acid.

The burette is filled with deci-normal permanganate, the zero point read off, even with the upper part of the liquid, as the meniscus is only seen with difficulty. 63 grammes of crystals of pure oxalic acid correspond to one litre of normal permanganate solution; hence 6.3 grammes to 100 C. C. normal; 0.63 grammes to 100 C.C. deci-normal. Weigh out 0.63 grammes oxalic acid place in a suitable flask, dissolve in distilled water, so as to have at least 50 C. C. and add 5 or 6 C. C. dilute H_2SO_4. Now heat gently, then place the flask under the burette and let a few C.C. of permanganate flow in. The mixture becomes rose red, but after a minute or two the color disappears entirely; if it remains longer, heat may again be applied, and more sulphuric acid added. As soon as the color has disappeared, more permanganate is added from the burette. The color now disappears more and more rapidly on each successive addition, until finally the rose-red color remains for several minutes. At this point the graduation is read off, the last drop deducted, and for each 1 C. C. permanganate used one per cent of pure oxalic acid is calculated.

Example 7. Ferric Chloride.

Ferric chloride, Fe_2Cl_6, is not directly affected by permanganate and can only be measured by the indirect method. This consists in adding to its solution a little hydrochloric acid and pure metallic zinc in small, thin fragments. The nascent hydrogen reduces the ferric chloride to ferrous chloride $Fe_2'''Cl_6 + H_2 = 2Fe''Cl_2 + 2HCl$. The yellow solution becomes, by this reduction, colorless, and does no longer redden potassium sulpho-cyanide. If this ferrous chloride be now treated with permanganate, in presence of H_2SO_4 and HCl it is reconverted into ferric chloride and the measure of permanganate used gives the quantity of iron salt present.

$$2KMnO_4 + 10Fe''Cl_2 + 10HCl + 3H_2SO = K_2SO_4 + 2MnSO_4 + 5Fe_2'''Cl_6 + 8H_2O.$$

Ferric chloride Fe'''_2Cl_6 has a molecular weight of 324.04, or when crystallized, $Fe'''_2Cl_6 + 12H_2O = 539.56$. Hence to ascertain the amount of anhydrous ferric chloride 3.24 grammes are placed into a flask dissolved in 100 C.C. water and a few drops of HCl and enough pure zinc in small fragments are added, to reduce to ferrous chloride. (Or a well amalgamated plate of zinc may be inserted). After reduction the surplus of zinc is removed, and some HCl and H_2SO_4 added. If the ferric chloride was pure 100 C.C. of deci-normal solution of potassium permanganate will be required to complete the reaction and give a red color to the solution. It is as well to operate with one-half the quantity or even less, to avoid refilling the burette. If one-tenth be used, then 10 C.C. permanganate are required for 100 per cent., and each $^1/_{10}$ C.C. indicates 1 per cent. of ferric chloride.

POTASSIUM DICHROMATE.

$K_2Cr_2O_7$ is an anhydrous salt, of molecular weight 293.78. (The U. S. P. assumes 294.8; Mohr, 295.12). Being a dibasic salt, one-half of this weight, 146.89 grammes, are used to make 1 litre of normal solution, or 14.69 for deci-normal. This would be the standard strength for all reactions in which the chromic acid remains undecomposed. In this strength the solution is used for determination of baryta. At present, however, it is hardly used for any other purpose than that of converting ferrous into ferric salts. This occurs by reduction of the dichromate to which **H_2SO_4** is added into chromic alum, while each molecule gives 3 atoms of oxygen to oxidize the ferrous salt.

$$K_2Cr_2O_7+4H_2SO_4=K_2SO_4.Cr_2(SO_4)_3+4H_2O+O_3.$$
$$6Fe''O+O_3=3Fe'''_2O_3.$$

Hence for such operations the action of one molecule **$K_2Cr_2O_7$** equals that of **3 O** or of 6 monatomic values, and the normal solution should contain $^1/_6 = 48.96$ grammes; the deci-normal 4.9 grammes. 100 C.C. normal solution are equivalent to 5.6 iron in any ferrous salt, for 100 C.C. deci-normal solution 0.56 iron must be employed, so that 1 C.C. shall correspond to 1 per cent.

No sufficient change of color marks the final point, nor can any indicator be added to the solution, but the end of the reaction must be shown by the method of spotting. For this purpose freshly prepared solution of pure ferri-cyanide of potassium is used, which, so long as ferrous salt is in the solution will give a precipitate of Turnbull's blue, but will only be colored brown by ferric salt. A number of separate drops of ferri-cyanide solution are placed on a porcelain plate. On nearing the final point, a small drop of the solution to be tested is taken out by a thin glass rod, and put into one of the drops on the plate. A blue spot will mark the presence of ferrous salt. As soon as this reaction no longer occurs, but a brown color is shown, the whole of the ferrous salt is converted into ferric, and the final point reached.

Example 8. Ferrous Sulphate.

This salt has the formula **$FeSO_4+7H_2O$** and its molecular weight is 277.45. By addition of **H_2SO_4** and oxygen it is readily converted into ferric sulphate **$Fe_2(SO_4)_3$**.

$$2FeSO_4+H_2SO_4+O = Fe_2(SO_4)_3+H_2O.$$

To analyze it, deci-normal solution of potassium dichromate is placed into the burette, and 2.78 grammes ferrous sulphate put into a beaker-glass of sufficient capacity, dissolved in about 50 C.C distilled water and about 20 C.C. dilute sulphuric acid (1 : 10) added. The standard solution is now dropped into it from the burette and repeatedly stirred with a thin, somewhat pointed glass rod, to mix well. Towards the end of the reaction the spotting upon the porcelain plate is done after every addition of the reagent until no more blue spots are made. The graduation is now read off and each C.C. corresponds to 1 per cent of crystallized ferrous sulphate.

The U.S.P. used 14.74 grammes dichromate in one litre, and weighs out 4.167 grammes of ferrous sulphate. Each C.C. of standard solution used, indicates 2 per cent.

IODIMETRY.

When solutions of iodine and of sodium hyposulphite are brought together in equivalent proportions, the iodine unites with one-half of the sodium of the hyposulphite and forms colorless sodium iodide and sodium tetrathionate:

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

Hence the normal solution of the one can be measured by equal number of C.C. of normal solution of the other. As the color of iodine is not sufficiently intense, starch-paste is used as an indicator, by means of which very minute portions of free iodine give a decided blue color. Other substances, such as SO_2, H_2S, As_2O_3, have a similar power of discharging the color of iodine by forming colorless compounds.

By means of the two companion solutions many analyses may be made either by the direct or indirect method. Thus we measure the strength of tincture of iodine directly by sodium hyposulphite, or that of sulphurous acid, or alkaline sulphites directly by iodine solution.

Free chlorine, or peroxides capable of evolving free chlorine from hydrochloric acid are measured by receiving the chlorine into a solution of potassium iodide, in which it liberates iodine, which is measured by sodium hyposulphite.

IODINE.

The atomic weight of $I = 126.56$. Pure dry iodine is easily obtainable, and its atomic weight is large, so that small errors in regard to its moisture are comparatively unimportant. Its normal solution contains 126.6 grammes in 1 litre. This, however, is seldom used, preference being given to deci-tormal solution, which contains 12.66 grammes in 1 litre. To dissolve this amount in water, 18 grammes of pure potassium iodide are dissolved in about 900 C.C. of water, the iodine is then added and dissolved by agitation, avoiding heat, and the litre-flask is then filled with water to the mark. The solution must be kept in small glass stoppered bottles, well sealed, in a dark place, and will then remain unchanged in strength for a long period. Weaker solutions are diluted from this when needed.

100 cubic centimetres of deci-normal iodine correspond to:

	Grammes.
I	1.266
$NaHSO_3$	0.520
$Na_2SO_3+7H_2O$	1.260
$Na_2S_2O_3+5H_2O$	2.480
H_2SO_3	0.500
SO_2	0.320
As_2O_3	0.495

It is used by adding to the substance to be tested a little starch-paste and adding the iodine solution until a permanent blue color is obtained.

SODIUM HYPOSULPHITE.

This salt crystallizes with 5 molecules of water: $\mathbf{Na_2S_2O_3+5H_2O}$. Its molecular weight is = 247.64. Its deci-normal solution contains 24.8 grammes in 1 litre. If absolutely pure salt cannot be procured, a stronger solution is made, and diluted to the standard by titration with deci-normal iodine. Of the pure salt 24.8 grammes are put into a litre flask, 2 grammes ammonium carbonate added, then water for solution, and lastly to fill up to the mark. The addition of ammonium carbonate helps to preserve the solution unchanged for a much longer time than it would remain without it.

Specimens containing iodine have starch-paste added to them and then the hyposulphite solution until the color disappears.

100 C.C. deci-normal solution of sodium hyposulphite correspond to:

	Grammes.
$Na_2S_2O_3+5H_2O$	2.480
I	1.266
Br	0.798
Cl	0.354
O in peroxides	0.798

Example 9. Tinctura Iodi. U. S. P.

This tincture contains 8 per cent of iodine. The pharmacopoeia prescribes that 6.33 grammes, (containing 0.5064 grammes iodine) mixed with 2 grammes of potassium iodide and a little starch-paste, should require, for complete decoloration, 40 C.C. of deci-normal solution of sodium hyposulphite.

Example 10. Liquor Potassii Arsenitis. U. S. P.

This corresponds in strength to 1 per cent As_2O_3.

In alkaline solution arsenites are converted by iodine into arsenates, the iodine forming an alkaline iodide. $K_3AsO_3+I_2+2NaHCO_3=K_3AsO_4+2NaI+2CO_2+H_2O$. Hence it is necessary that a sufficiency of sodium bi-carbonate be added. 24.7 grammes of Fowler's solution are boiled with 0.5 grammes of $NaHCO_3$, diluted with 100 C.C. of water and some starch-paste added. Deci-normal iodine solution is now added until a light blue color becomes permanent. For the full strength of 1 per cent, it is requisite that 50 C.C. should be used. The U. S. P. allows a deviation of 1.5 C.C. less. 100 C.C. iodine, decinormal, correspond to 0.495 grammes As_2O_3. (¼ molecular weight = 49.5).

Example 11. Liquor Sodae Chloratae. U. S. P.

Labarraque's solution.

The active ingredient in this solution is sodium hypochlorite, $NaOCl$, whose Cl should amount to 2 per cent of the solution. 100 C.C. hyposulphite, deci-normal, corresponds to 0.354 grammes chlorine. Hence 35.4 grammes of the Labarraque's solution containing 1 per cent require 100 C.C. hyposulphite; or 17.7 grammes containing 2 per cent, will also require 100 C.C.; or one-half of this = 8.85 grammes require 50 C.C. of sodium hyposulphite, deci-normal.

As chlorine cannot be measured directly, potassium iodide is added and some hydrochloric acid and starch-paste. The free chlorine liberates iodine and this is measured as before by addition of hyposulphite until decoloration. Put into a suitable flask 8.85 grammes of Labarraque's solution, add 2.6 grammes potassium iodide, dissolved in about 200 C.C. of water; then add about 25 C.C. hydrochloric acid and some starch-paste. Now let the deci-normal hyposulphite solution flow into it from the burette until, on agitation, all the color is discharged. It should require 50 C.C.

PRECIPITATION ANALYSES.

SILVER NITRATE.

The molecular weight of $\mathbf{AgNO_3}$ is 169.58. Hence its normal solution would contain that number of grammes in 1 litre. But while the deci-normal and centi-normal solutions are frequently used, the normal solution is scarcely ever needed. To make deci-normal solution dissolve 16.96 grammes fused silver nitrate in pure distilled water, so as to fill the litre flask to the mark. It must be preserved in glass stoppered bottles, and carefully guarded against dust, while filling the burettes. Silver nitrate forms precipitates with the compounds of **Cl, Br, I, CN, CNS,** etc., and by means of various devices, the final point may be accurately determined, and the quantity of these substances calculated. In the case of **Cl, Br,** and **I** the precipitate is not only heavy, but has also the property of forming coherent, curdy masses, which subside and after some time, leave a clear supernatant liquid, in which a further precipitation may be readily seen. This coherence takes place more promptly when the liquid containing the precipitate is strongly agitated. As in either case the clearing of the liquid takes some time, indicators are often resorted to. Yellow potassium chromate, $\mathbf{K_2CrO_4}$, is the one mostly employed, when **Cl, Br** or **I** are to be determined. This forms with $\mathbf{AgNO_3}$ an intensely red silver chromate. It is decomposed by soluble chlorides, etc. and hence only forms on the additionof silver nitrate to a liquid in which all the chlorine, etc., has been converted into insoluble silver salt. A permanent red of the opaque mixture indicates the completion of the precipitation of **Cl, Br** and **I.**

When **CNS** is to be determined by $\mathbf{AgNO_3}$, the sulpho-cyanide is colored red by ferric sulphate; as soon as all of the **CNS** has been precipitated as white silver sulpho-cyanide, the red color disappears. Reversing these operations silver may be determined by a standard solution of sulpho-cyanide, or of chloride, etc.

SODIUM CHLORIDE.

This forms the companion solution to silver nitrate. It is made from pure **NaCl** and is also most frequently used in deci-normal solution, containing 5.84 grammes in 1 litre. It is generally made by dilution of a stronger solution with water, so as to correspond accurately with the silver nitrate. Sometimes a saturated solution of **NaCl** is made, and of this 18.36 C.C., diluted to a litre, will come at once very near to the right titre.

MERCURIC CHLORIDE.

This is used as deci-normal solution for titration of **KI.** $HgCl_2$ has a molecular weight of 270.45; as it contains **2Cl,** one-half is taken, and for deci-normal solution 13.52 grammes are dissolved in water to form 1 litre. When brought together with **KI** it forms a precipitate of HgI_2 of intense, scarlet color. This dissolves in **2KI,** forming a double salt. Hence if $HgCl_2$ is brought together with **4KI,** there is formed $HgCl_2+4KI=HgI_2.2KI+2KCl$. There is a complete solution of $HgI_2.2KI$ but as soon as even a single drop of $HgCl_2$ is added in excess of the quantity necessary to convert one-half of the **4KI** present into the double salt, then a red precipitate of HgI_2 remains undissolved, and the exact measure of one-half of the **KI** present is indicated.

Example 12. Potassium Cyanide.

KCN forms with silver nitrate solution **AgCN,** insoluble in water, but easily soluble in solution of potassium cyanide, forming a double salt. $2KCN+AgNO_3=AgCN.KCN+KNO_3$. Hence if silver nitrate solution be added from a burette to a solution of **KCN,** no precipitate will fall, until after half of the cyanide of potassium has been converted into silver cyanide. The quantity of pure salt in a commercial specimen can be thus easily obtained. The molecular weight of **KCN** is 65.01. The quantity necessary to form **AgCN** with 100 C.C. of deci-normal silver nitrate is 0.65 grammes, which with 50 C.C. will form soluble **AgCN.KCN.** The graduation is read off as soon as a permanent turbidity remains after shaking. If the salt is pure, there will be no precipitate until 50 C.C. have been exceeded by a drop or two; if water or other impurities are present, less will be used, and the percentage will be known by doubling the number of C.C. of silver solution used. Hydrocyanic acid may be determined by this method, by saturating it first with **KOH.** It requires 0.27 grammes of **HCN** to correspond to 50 C.C. of silver nitrate.

Example 13. Potassium Iodide.

This may be determined by silver nitrate, with an indicator of potassium chromate, but only when it is entirely free from **Cl.** We use mercuric chloride in deci-normal solution, to avoid any error arising from the presence of chlorides. The molecular weight of **KI** is 165.58. Hence for complete precipitation as $\mathbf{HgI_2}$ there are required 1·66 grammes for 100 C.C. of mercuric chloride solution. It is preferable however not to read off at the completion of the precipitation, but at the first formation of the precipitate, as soon as the soluble double salt begins to be decomposed again by addition of $\mathbf{HgCl_2}$. Therefore 1.66 grammes will require 50 C.C. mercuric solution to keep the double salt in solution and any excess of this will form a precipitate. The number of C.C. is read off and doubled to give the per centage.

Example 14. Potassium Bromide.

The molecular weight of **KBr** is 118.79; hence of the pure salt 1.19 grammes are required to convert 100 C.C. deci-normal silver solution into **AgBr. KCl** has a molecular weight of 74.39; hence 0.74 grammes of **KCl** would correspond to 100 C.C. of $\mathbf{AgNO_3}$. If therefore a considerable quantity of **KCl** is present in **KBr** there will be more then 100 C.C. deci-normal silver solution used for 1.19 grammes of substance. (174 C.C. if that much pure **KCl** is taken.) Hence an excess of silver solution used indicates **KCl** as impurity.

The silver solution is put into the burette and zero point and jet accurately adjusted; 0.6 grammes of potassium bromide are put into a flask, dissolved in 10 C.C. of water and about $\frac{1}{2}$ C.C. of solution of yellow potassium chromate added. The silver is then run in until the red, which first only surrounds the entering drop, and disappears on shaking, remains visible, as an orange coloration, throughout the mass. The two last drops are deducted from the silver solution used and if the bromide is pure, 50 C.C. should be used, corresponding to 100 per cent. A less number indicates moisture or other impurities, a higher number of C.C. silver solution used shows that chlorides are present.

In similar manner iodides and chlorides may be determined, weighing out the one-hundreth part of the molecular weight in grammes of the substance to be determined; then every 1 C.C. of deci-normal silver solution indicates one per cent of the substance sought.

If **Sodium chloride** is to be determined in **urine**, 5.84 C.C. of urine are measured out and tested with deci-normal silver nitrate. In this however the pigment interferes with the accuracy and the result is about 10 per cent too high.

For accurate results the pigments must be destroyed by measuring 5.84 C.C. urine into a capsule of platinum or porcelain, adding 0.2 gr. pure potassium nitrate, dessicating and then fusing the mass. The residue is dissolved in water and gives accurate results on titration. Each C.C. silver solution corresponds to 1 gramme sodium chloride in 1 litre of urine.

Example 15. Silver Nitrate.

Lunar Caustic.

This salt is liable to be diluted with considerable quantities of potassium nitrate. If pure it has no water of crystallization and its molecular weight is 169.58.

The burette is filled with deci-normal sodium chloride. 0.85 grammes of the lunar caustic are put into a flask, dissolved in some distilled water and ½ C.C. yellow potassium chromate solution is added. This produces a deep red precipitate, which begins to decompose, when the sodium chloride is added from the burette and whose color is entirely discharged as soon as all the silver is converted into chloride, which with pure salt will require 50 C.C. Each C.C. corresponds to 2 per cent of silver nitrate.

The U. S. P. recognizes different grades, the pure, the dilute, which contains 50 per cent of potassium nitrate, and the fused, which contains about 5 per cent of silver chloride.

SPECIAL VOLUMETRIC PROCESSES.

FEHLING'S SOLUTION.

To determine the quantity of glucose in a specimen various processes have been proposed, but among all of them that by **Fehling's test solution** deserves the first place.

Glucose, $C_6H_{12}O_6 + H_2O$, has a molecular weight of 197.54, or anhydrous 179.58.

As already stated (organic example 4,) glucose has the property to reduce, in alkaline solutions, cupric to cuprous oxide. This occurs in the proportion of 1 molecule of glucose to 5 molecules of cupric salts. If cupric sulphate $CuSO_4 + 5H_2O$ is decomposed 5 x 248.79 or 1243.95 parts are reduced by 179.58 parts of $C_6H_{12}O_6$ (anhydrous glucose.) This in simpler proportion gives 6.927 grammes cupric sulphate reduced by 1 gramme glucose. This is the quantity employed in the U. S. P. but to make it correspond to the ordinary standard, it is also directed that only 200 C.C. of solution should be made of it instead of one litre. Fehling's solution uses 5 times that quantity or 34·635 grammes of crystallized cupric sulphate for one litre of solution, capable of decomposing exactly 5 grammes of anhydrous glucose. The test solution is prepared as follows:

In a flask 34.635 grammes of pure cupric sulphate are dissolved in about 160 C.C. of distilled water. In the litre flask 150 grammes of neutral potassium tartrate (or 100 grammes of Rochelle salt) and 36 grammes of caustic soda, are dissolved in from 600 to 700 C.C. of distilled water. To this the copper solution is gradually added, with constant agitation to redissolve the precipitate formed at first, the bottle is rinsed with distilled water, which is also added to the mixture, and finally the litre flask is filled with distilled water to the mark and the solution thoroughly mixed. It is best preserved in a dark place, in small glass stoppered bottles, sealed with paraffine.

1000 C.C. correspond to 5 grammes glucose.
100 C.C. " " 0.5 gr.
10 C.C. " " 0.05 gr.

Example 16. Glucose.

Grape Sugar.

Weigh out 1.0 gramme of grape sugar and dissolve in 500 C.C.

of water. Fill with some of this the 50 C.C. burette and adjust it so that its jet will be directly over the surface of a porcelain dish of at least 100 C.C. capacity, which is supported on the iron lampstand over a Bunsen burner (or alcohol lamp). Into the porcelain dish put, by means of a 10 C.C. pipette, 10 C.C. of Fehling's solution. Put into it likewise a narrow strip of window glass about 100 Mm. long and about 10 to 12 Mm. broad, to be used as a stirring rod. Let the porcelain capsule rest upon a small iron ring so that the lamp, which is placed sufficiently far below, and with a very small flame, cannot heat the sides of the dish above the liquid. Now apply heat carefully until the Fehling's solution begins to show signs of boiling. Then let some C.C. of the sugar solution flow in from the burette, so as

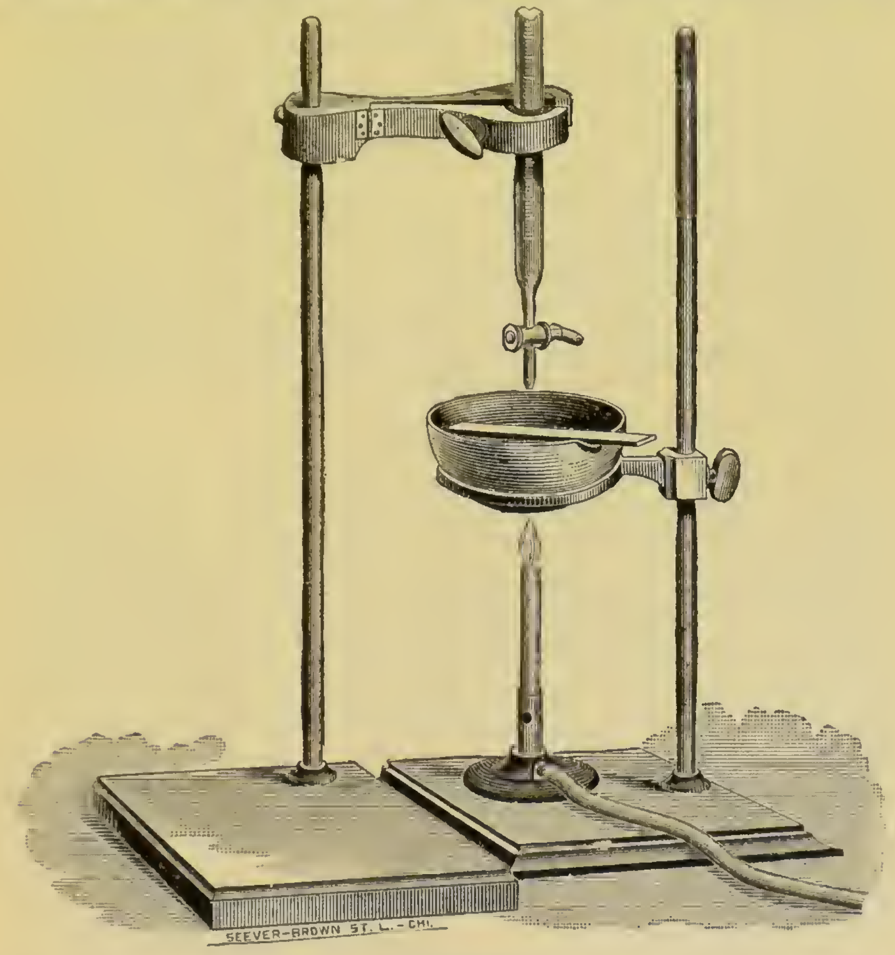

SEEVER-BROWN ST. L.-CHI.

FIG. 12.

to spread over the flat stirring rod. A small cloud of yellow cuprous hydrate will form on the surface. This is removed by stirring slightly, the liquid permitted to reach the incipient boil and more sugar solution added. Gradually the deep blue color of the cupric solution will disappear and the final point is to be observed either by the cessation of the formation of the yellow cloud on adding a few more drops of sugar solution, or by the absence of blue from the color of the supernatant liquid. Or else by spotting with a drop of the liquid upon a white porcelain plate containing drops of solution of potassium ferrocyanide mixed with acetic acid. So long as copper remains in solution it will make a brown spot in the drop of the reagent. Either of these methods allows of equal accuracy, when the eye is once practiced to discern the final point. The graduation is then read off and the calculation made. In the present case we have used 25 C.C. of glucose solution. These 25 C.C. contain the quantity capable of being decomposed by 10 C.C. Fehling's solution=0.0 5 gr. hence 5 C.C. contain 0.01 and the 500 C.C. in which the sugar was originally dissolved contain 100 times as much or 1.0 gramme. Therefore the glucose employed was pure, containing 100 per cent of glucose. If it had been less pure, more C.C. of it would have been needed to decompose the 10 C.C. Fehling's solution.

When glucose has to be determined in **urine,** some preparation is necessary to remove coloring matter, and other substances, capable of interfering. Measure 100 C.C. of urine, put it into a 200 C.C. flask, add some milk of lime or strong barytawater, and fill up to the mark with water. Filter the mixture and fill a burette with it. Now proceed exactly as with the sugar solution before. Suppose 100 C.C. have been used to decompose 10 C.C. Fehling's solution. As the urine has been diluted to double the quantity, these 100 C.C. diluted urine correspond to 50 C.C. undiluted and contain 0.05 gr. glucose, the quantity indicated by 10 C.C. Fehling. Hence 50 C.C. to 100 C.C., as 0.05 grammes glucose to 0.10. The urine contains $^1/_{10}$ per cent of glucose.

Cane sugar may be determined by the same method by inverting. (Compare organic example 5.) 9.5 grammes dry cane sugar dissolved in 700 C.C. water, to which 5 C.C. hydro chloric acid has been added, are, by boiling, changed to 5 grammes dextrose, and 5 grammes laevulose; which reduce Fehling's solution in almost the same proportion as 10 grammes glucose would do. The acid solution must be neutralized by **KOH** and diluted to 1 litre. The quantity of glucose found is reduced to that of cane sugar; originally present, in proportion of 100:95.

Mercuric Nitrate:

An empirical solution of mercuric nitrate is made for the determination of urea, according to Liebig's method, by dissolving 77.2 grammes pure mercuric oxide in as little nitric acid as possible, and diluting to 1 litre. Each 1 cubic centimeter corresponds to 0.010 grammes urea. When mercuric nitrate is gradually added to a dilute solution of urea and the free acid occasionally saturated by sodium carbonate; a flocculent white precipitate is formed containing 1 molecule of urea and 2 molecules of mercuric oxide. Urea $= \mathbf{CO(NH_2)_2} = 59.97$. Mercuric oxide$=\mathbf{HgO}=215.67$. As soon as all the urea in the solution is precipitated, the addition of $\mathbf{Na_2CO_3}$ produces a yellow precipitate of **HgO**; where before a white one had fallen:

Example 17. Urea.

Put 10 C.C. of solution of urea into a small flask, from the burette add mercuric nitrate solution, as long as it is evident that a precipitate falls. As soon as this is no longer plainly discernible, pour a few drops of the mixture into a watch-glass and add to it a few drops of sodium carbonate solution. If a white precipitate forms; pour the contents of the watch-glass back into the flask; add another $\frac{1}{2}$ C.C. and try again on the watch-glass. As soon as the addition of $\mathbf{Na_2CO_3}$ produces a yellow precipitate of mercuric oxide; the experiment is ended and the graduation is read off. Each C.C. of mercuric nitrate used corresponds to 0.010 grammes of urea. As 10 C.C. urea solution are used, the number of C.C. mercuric nitrate divided by 10 gives the number of per cent of urea in the solution.

In urine used without previous preparation, the presence of phosphates and of sodium chloride occasions a small error; which however for ordinary purposes may be neglected. If great accuracy is desirable; the chlorine must be removed by silver nitrate, and the phosphoric acid by magnesia, or baryta-water.

Example 18. Phosphoric Acid.

The salts of the tri-basic (ortho-)phosphoric acid, $\mathbf{H_3PO_4}$, may have one, or two, or all three of the hydrogen atoms replaced by a monatomic base. Those containing 1 atom of an alkaline base give a neutral reaction with color tests, those containing more than 1 atom show an alkaline reaction.

On this property Stolba's alkalimetric method for measuring the quantity of phosphoric acid is founded, which is adapted to the determination of all soluble phosphates, and is especially applicable to those occurring in urine.

The soluble phosphates are converted into insoluble **magnesium-ammonium phosphate, $\mathbf{Mg.NH_4.PO_4}$,** by precipitating them with a mixture of magnesium chloride (or sulphate), ammonium chloride, and ammonium hydrate. The precipitate is separated by filtration, washed with water, containing a little ammonia, and transferred to a beakerglass.

A few drops of an indicator are then added, for which tincture of cochineal is recomended by Stolba.

Normal solution of hydro-chloric acid is now added from a burette until the indicator shows acid reaction. This occurs as soon as even a slight excess of acid has been added above the quantity corresponding to two thirds of the bases. The cochineal tincture then changes from violet to yellowish-red. Two molecules of hydrochloric acid used, correspond to one molecule of ortho-phosphoric acid. The molecular weight of $\mathbf{H_3PO_4}$ is 97.80. Hence if 97.8 grammes of urine (=98.09 C.C. if of specific gravity 1.025) are precipitated by the magnesia mixture and the precipitate treated as above, every 2 C.C. of normal hydrochloric acid used, indicate 10 per cent of phosphoric acid. Or if deci-normal hydrochloric acid is used, every 2 C.C. indicate one per cent.

Tincture of cochineal is made by digesting, for a few days, 4 grammes of the whole insect with a mixture of 50 C.C. of alcohol and 200 C.C. of water, and decanting the clear liquid.

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ERRATA.

Page.	Line.	For	Read.
16	12 from top,	phenolphthalleine,	phenol-phthaleine.
20	23 "	VIII	VII.
22	9 "	glycerlne	glycerine.
22	21 "	$4MgCo_3$	$4MgCO_3$.
25	28 "	foliowing	following.
26	9 "	phoshporic	phosphoric.
32	14 "	XXII	XXI.
32	27 "	ziuc	zinc
35	4 from bottom,	$PbC_2H_3O_2$	$Pb(C_2H_3O_2)_2$.
45	10 and 17 "	Na_4SiO_4	Na_2SiO_3.
51	3 "	XLII	XLIII.
51	3 "	$L\ _2CO_3$	Li_2CO_3
89	4 "	Cn_2I_2	Cu_2I_2
94	3 "	$H\ O_2$	H_2O.
95	12 "	molbydic	molybdic.
95	4 "	$M\ O_3$	MoO_3
107	6 from top,	molbydic	molybdic.
107	12 "	is	in
118	7 from bottom,	centimenter	centimeter